MOLECULAR ENERGY TRANSFER

IN GASES.

BY

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ABSTRACT OF THESIS

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Title of Thesis MOLECULAR ENERGY TRANSFER IN GASES.

Vibrational energy transfer in gases has been studied using the ultrasonic velocity technique. The work is in two parts; in the first the effects of inert gas atoms and deuterium on relaxation in carbon dioxide have been studied, and in the second, similar studies were made using methane with additives.

The efficiencies of inert gases for de-exciting CO_2 turn out to be less than expected by theory, and an explanation is sought in terms of "softer" intermolecular interactions than those assumed by the theory. Deuterium is approximately four times more efficient than helium, and a mechanism involving the transfer of vibrational energy from CO_2 into the rotational levels in deuterium is put forward.

It is assumed that vibrational energy in methane is transferred via the rotational modes into translation. Helium and oxygen are found to be approximately half as efficient as methane itself, and this is explained in terms of vibration-rotation transfer within the same methane molecule.

Use other side if necessary.

I N D E X

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CHAPTER 1.

I N T R O D U C T I O N.

The rate at which vibrational energy in molecules is transferred by collisions into translational modes is studied by a variety of techniques, the majority of which measure the appearance of the energy in the translational modes rather than its disappearance from vibrational modes. Ultrasonic interferometry in particular supplies information about the rate of re-appearance in translational modes of energy from all possible vibrational modes in the gas. At first sight, this suggests that detailed analayses of the mechanism of energy transfer are beyond the scope of the technique, which is thus restricted to fairly simple comment about the overall vibration-translation (VT) process. However, information about the fine structure of this overall process comes from two sources, namely from direct measurements of the relaxing specific heat, and indirectly from a comparison of results for a series of molecules and from studies in the deviation from a series which the inclusion of a new parameter produces. Measurements of the relaxing specific heat of a wide range of molecules have established that in the majority of cases all the vibrational modes relax together because the relaxing specific heat contains the contributions of all vibrational modes in the molecule; in a few cases two separate relaxation regions have been detected, each region of which corresponds to a separate overall (VT) process involving a set of modes. Thus in the case of SO_2 the two upper modes relax together at a different rate from that of the lowest mode. It has been concluded from these observations that vibrational energy transfer between vibrational modes in a molecule is generally very rapid, so that equilibration with translational modes occurs as a single process. Direct experimental

measurements have thus revealed something of the fine structure of the overall process, but reveal nothing about the final step, namely the transfer of energy into translational modes, which may or may not have a fine structure. At this point the second source of information becomes dominant. Landau and Teller (1) working on the assumption that there is no further fine structure have established a theoretical relation for the transition probabilities in VT transfer in terms of the size of the transition, the characteristics of the encounter between collision partners, and the translational temperature. Information over a wide range of parameters has shown a functional agreement with the Landau-Teller expression, and so establishes the soundness of the assumption which is made. On the other hand, there are related groups of molecules in which the rational pattern is not discernable, and it is reasonable to suspect that the assumption may not be valid for this group. A scheme may then be proposed based on a common characteristic of the group which could reasonably be expected to influence energy transfer. This is well illustrated in a recent paper by Moore (2), which extends to a wide range of molecules a theory of vibration-rotation energy transfer first proposed by Cottrell and Matheson (3). Moore observes that many large, slowly rotating molecules follow the Landau-Teller predictions and thus establish a norm for which simple VT transfer is a satisfactory explanation. He then observes that some molecules with large speeds of rotation, such as CH_4, SiH_4, which were first studied by Cottrell and Matheson, show deviations from the Landau-Teller group, being in all cases more efficient than them. Using this common factor as a basis, he extends and develops the idea of a vibration-rotation process within the overall VT scheme. He finds that the Landau-Teller expression modified by Cottrell and Matheson to include rotational rather than translational speeds of encounter provides better agreement with experiment over a wide range of parameters, and thus establishes the intermediate role of rotational modes in

the equilibration of vibrational energy with kinetic energy.

It is now proposed to examine from interferometric work four characteristics of the development of concepts about the structure of the de-excitation process in energy transfer; they are the firm establishment of VT behaviour over a range of parameters, the detection of significant deviations from this behaviour, the proposal of a qualitatively reasonable explanation, and the translation of this into a mathematical form which can quantitatively explain the deviations observed. The VT process may be defined as the transfer of vibrational energy, which may arise from more than one mode, into kinetic energy in homo - or hetero -molecular collisions without the intervention of other internal modes. The Landau-Teller expression, which does not provide an explicit relation for the transition propability of an encounter, nevertheless provides a functional relation through its exponential term which is a quantitative description of the process, and thus provides a basis on which to ascertain the applicability of the process to a particular molecule. The first simple but important step is to establish that no other scheme is physically reasonable in this instance; then functional agreement between experiment and the Landau-Teller expression is a satisfactory criterion for the VT process. However, comparison of a single parameter can lead to false conclusions; for example, although the temperature dependence of relaxation in CO_2- H_2O mixtures is in the opposite sense to that predicted by the Landau-Teller expression, a VT scheme is believed to be operative, and the deviation is attributed to factors affecting the dynamics of the encounter which are not accounted for by the theory rather than the structure of the de-excitation scheme. On the other hand, experiments in which the reduced mass of an encounter is varied at a fixed temperature by the use of inert gas collision partners would provide only a limited range over which to establish a VT process. Milliken (4) has approached the problem by choosing for study molecules and collision pairs in which only VT transfer is to be expected, such as diatomic molecules and inert gases, and has compared their temperature dependencies

with the Landau-Teller prediction and found good agreement. Moore has observed a rational pattern in a large group of molecules in accordance with Landau-Teller predictions relating to mass and vibration frequency. As there is no direct confirmatory experimental evidence for a VT process containing no fine structure, the concept possesses a certain arbitrary nature, and can be termed the most probable process for a particular molecule which conforms to the accepted criteria.

These criteria necessarily define the means by which other processes are detected. Initially the observation that the experimental transition probability for a molecule lies significantly outside a group of molecules in which VT transfer is considered operative indicates that a process other than this may be present; moreover, it allows a distinction to be drawn between the presence of a possible new scheme and a situation which could be explained by refinements to the theory, because the incorporation of refinements would restore agreement between the experimental results and the comparison group. There exist in the literature examples of the detection of significant functional differences between the Landau-Teller theory of VT transfer and experimental results in both pure gases and mixtures which have established the existence of new transfer schemes. To do this molecules must be chosen for comparison with the molecule in question in such a way that the parameter which is thought to be responsible for the observed effects be pin-pointed, and parameters which are conceptually vague in the explicit form of the Landau-Teller theory be eliminated. In pure gases, studies in isotopic substitution represent significant detections of deviations from the VT process. Cottrell and Matheson compared the relaxation times of methane and tetradeuteromethane and found the former to be shorter, although conventional theory predicted that the effect of the smaller vibrational quantum in CD_4 would outweigh the effect of its larger mass, making CD_4 more efficient. In this

comparison they eliminated the concept of the reduced mass of the oscillator, the problem of representing the sharpness of the interaction during a collision, and the possibility that a refinement of existing theory might restore agreement with the Landau-Teller predictions, because in all three respects the molecules are almost identical. The significantly greater efficiency of CH_4 is thought to be due to the faster rotating hydrogen atoms, which allow rapid transfer of vibrational energy into rotational modes and thence into translation.

Hudson, McCoubrey and Ubbelohde (5) have detected significant deviations from the concept of fast internal equilibration between vibrational modes in C_2H_4 and C_2D_4. Uncertainty in the interpretation of the reduced mass of the oscillator in molecules as complex as C_2H_4 defines a range within which VT transfer is a reasonable explanation, but this range is considerably reduced when C_2H_4 is compared with C_2D_4 to which the same range applies. The authors define the limits of the theoretical ratio $P_{10}C_2H_4$ / $P_{10}C_2D_4$ for VT transfer as 1/7 - 1/3.5 but find experimentally a ratio of 1/2, which points to a process other than simple VT transfer. However, it does not follow that there is a unique interpretation of deviations from VT behaviour; in fact two explanations exist for the C_2H_4 - C_2D_4 results. Hudson, McCoubrey and Ubbelohde suggest that the explanation of the reduced efficiency of C_2D_4 over C_2H_4 lies in the rate at which modes equilibrate internally compared with the final VT process. In C_2H_4 they calculate using the expression derived by Tanczos (6) for vibration-vibration (VV) transfer that the process:-

$$\underset{943\ cm^{-1}}{C_2H_4} + C_2H_4 \longrightarrow \underset{810 cm^{-1}}{C_2H_4} + C_2H_4$$

is thirteen times faster than C_2H_4 810 $cm^{-1} \longrightarrow$ KE, which is therefore rate determining, whereas in C_2D_4 the process 726 $cm^{-1} \longrightarrow 584 cm^{-1}$ is only twice as fast as 584 $cm^{-1} \rightarrow$ KE. In this case the overall

relaxation time will be the weighted mean of the two processes and will therefore be longer than the simple 584 cm^{-1} → KE. relaxation time. They reinforce their argument by finding very good agreement between the Tanczos expression and experiment for the VV process:-

$$\underset{810\ cm^{-1}}{C_2H_4} + C_2D_4 \longrightarrow C_2H_4 + \underset{584\ cm^{-1}}{C_2D_4}$$

Moore explains the relative efficiencies of C_2H_4 and C_2D_4 in terms of the rotation hypothesis first suggested by Cottrell and Matheson, whereby the enhanced efficiency of the faster rotation of hydrogen atoms around the double bond compared to the deuterium atoms partly compensates for the effect of the relative sizes of the vibrational quanta. Both theories possess the two characteristics noted earlier; that is, both are qualitatively reasonable and have the backing of mathematical models, respectively the Tanczos expression and a modified version of the explicit form of the Landau-Teller expression derived by Cottrell and Ream (7). Any attempt to decide between the two explanations on existing evidence raises the problem of the relative status of the mathematical models employed, and one can conclude that the model with which there is more general experimental agreement is the more probable process.

Wor't on the mixtures represents a slightly different approach to the problem. Here collision partners can be carefully chosen to fit the exact conditions under which a new scheme is thought likely to operate without introducing factors which could obscure the result. Thus mixtures can be made up in which near resonant vibration transfer is possible without at the same time introducing a reduced mass or interaction effect to which catalytic activity could be attributed. The converse is in fact often true; that is, experiments can be designed in which extra effects cause a change in efficiency in the opposite sense to vibration-translation parameters. In addition, information can be obtained directly from measurements of the relaxing specific heat

and the dependence of relaxation times on the mole fraction of additives. The recent work of Lambert and his co-workers (8) provides examples of all these points; They have chosen collision partners between which near vibrational resonances exist, such as CF_4 (435 cm^{-1}) and C_2F_4 (220 cm^{-1}) and have studied their behaviour in terms of the following de-activation scheme:-

A^+	+	A	→	A	+	A	+ $(KE)_1$	1
A^+	+	B	→	A	+	B	+ $(KE)_1$	2
A^+	+	B	→	A	+	B^+	+ $(KE)_2$	3
B^+	+	B	→	B	+	B	+ $(KE)_3$	4
B^+	+	A	→	B	+	A	+ $(KE)_3$	5

where the star + represents vibrational excitation ; suffixes distinguish the different amounts of energy transferred to translation. Two classes of behaviour were distinguished by direct experiment, namely single dispersion of the total vibrational specific heat with a relaxation time not linearly dependent on the mole fraction of (B), and double dispersion corresponding to separate vibrational relaxation of B and A, the latter with a linear dependence on (B). They reason that the first observation can be explained in terms of a very rapid near resonant process (3) followed by the rate determining process (4) through which the total vibrational specific heat equilibrates with translational modes. Processes(1) and (2) were neglected because they cannot supply vibrationally excited B which is required by the mole fraction dependence, and because in some instances process (2) should be slower than process(1) from mass and interaction effects as predicted by the Landau-Teller expression. Similarly in the second case, (1) and (2) can be neglected; but now (3) is slower than (4) although A still equilibrates its vibrational energy by VV transfer through B. By virtue of its use of direct experimental information to demonstrate new schemes, this work provides the most convincing

demonstration of vibration-vibration energy transfer by ultrasonic means published so far.

The present work can be divided into two parts. In the first the effect of inert gas atoms and diatomic molecules on relaxation in carbon dioxide is studied, and in the second similar studies are made using methane. In both cases attempts have been made to explain the observations bearing in mind the points discussed so far.

It is assumed that vibrational energy transfer in carbon dioxide occurs as a single VT process, because its temperature dependence agrees with the Landau-Teller theory and because it can be grouped with a large number of molecules for which the same scheme applies. Collisions between carbon dioxide and inert gas atoms are therefore most likely to result in simple VT transfer, and significant deviations from the Landau-Teller predictions which have been detected are therefore explained by refinements to existing theory. However, in collisions between CO_2 and deuterium there are reasons, consistant with the results for inert gases, to believe that a scheme involving the transfer of vibrational energy from CO_2 into rotational levels in deuterium may be operative.

Studies in methane relaxation present different problems because it is assumed that vibrational energy is transferred via the rotational modes into translation. When the effect of additives is considered, the situation turns out to be more complex than in the case of CO2 and inerts. For instance, collisions between methane and helium could result either in vibration-translation transfer or in vibration-rotation transfer within the same methane molecule, and if oxygen is substituted for helium the possibility of transfer into its rotational modes must also be considered.

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CHAPTER 2.

SOUND PROPAGATION AND RELAXATION IN GASES.

Energy is transferred between pairs of molecules during collisions in such a way that a dynamic equilibrium is maintained between all the modes of motion in a gas. When the translational temperature is disturbed, equilibrium is restored at almost every collision between translational and rotational modes, but only one in fifty thousand may be effective in transferring vibrational energy into translation. The ultrasonic interferometer provides a means of producing a variable periodic heating and cooling of translational modes in a gas, and a means of detecting the accompanying changes in its vibrational and rotational modes. Both are achieved by the use of sound waves, which are propagated through a gas as a series of compressions and rarefactions, at a speed which the interferometer can measure and which depends on the total specific heat of the gas. The time taken for the re-distribution of translational energy amongst the internal modes is called the "relaxation time". If the period of compression and rarefaction is reduced sufficiently, then only those molecules which undergo the rare effective collision will be able to equilibrate their vibrational modes with the new translational temperature, and follow its cyclic changes. There will be a value of the period of compression and rarefaction for which a negligible number of molecules make the effective collision which allows them to follow the fluctuations in translational temperature. At this point the vibrational mode has become opaque to the cyclic flow of energy in the gas and makes no contribution to its specific heat. The inflexion point in variation of specific heat with frequency corresponds to the frequency of energy fluctuations with which the average molecule just fails to keep up, and defines the average relaxation time. Outside this critical frequency range, the "dispersion region", the specific heat of the gas is independent of frequency.

Thus the measurement of vibrational relaxation times in the ultrasonic interferometer reduces to the determination of the frequency dependence of the specific heat, conveniently measured as the velocity of sound, in the dispersion region.

The following section expresses these general ideas in mathematical form. The velocity of sound in an ideal gas is given by the expression:-

$$V^2 = \partial p/\partial \rho$$

p = pressure

ρ = density

The process is adiabatic and isentropic, so that the expression

$$pV^{\gamma} = \text{constant}$$

also applies.

Thus $$V^2 = \gamma p/\rho$$

$$= RT/M\ (1 + R/C_v)$$ γ C_v = specific heat at constant volume, (1)

In order to correct for non-ideality in gases, the expression is re-derived from the equation of state of a real gas, given approximately by:-

$$PV = RT + Bp \qquad (2)$$

where B is the second virial coefficient.

Equation (1) can then be written:-

$$V^2 = \frac{-V^2}{M}\left(\partial p/\partial V\right)_s$$

$$= -\left(\gamma V^2/M\right)\left(\partial p/\partial V\right)_T$$

Combining this with (2) gives the velocity of sound in a real gas:-

$$V^2 = \gamma/M(RT + 2Bp)$$

which can be further arranged for extra clarity to:-

$$\frac{V^2}{V_{id}^2} = \frac{\gamma}{\gamma_{id}}\left(1 + \frac{2Bp}{RT}\right)$$

where the suffix "id" means ideal.

It now remains to derive an expression for γ real. The following relations have been derived by Roberts (9)

$$Cp = Cp_o - TpB''$$
$$Cv = Cv_o - p(2B' + TB'')$$

where B' and B'' are the first and second derivatives with regard to temperature of virial coefficient.

therefore $\gamma = \gamma id \left(1 + 2pB'/Cvo + pRTB''/Cvo\,Cpo\right)$

therefore $$V^2 = \frac{\gamma idRT}{M}\left(1 + \frac{2p}{RT}\left(B + \frac{RTB'}{Cvo} + \frac{R^2T^2B''}{2Cvo(Cvo+R)}\right)\right)$$
$$= Vid^2\,(1 + 2Sp/RT)$$

thus $$V = Vid\,(1 + Sp/RT)$$

THE RELAXATION EQUATION .

Consider the relaxation of a vibrational mode ν in which only the ground and first excited states are appreciably populated with populations No, N1 respectively.

At equilibrium

$$N_1 = \bar{N}o \exp - (h\nu/RT)$$

The rate of formation of excited molecules can be expressed as:-

$$\frac{dN_1}{dt} = fo_1No - f_1oN_1$$

where fo_1 and f_1o are the rate constants for excitation and de-excitation respectively.

At equilibrium $$\frac{dN_1}{dt} = \frac{dNo}{dt} = 0$$

so that $$fo_1/f_1o = \exp. - (h\nu/RT)$$

If the system is perturbed in such a way that N_1 increases by an amount ΔN_1,

$$\frac{d\Delta N_1}{dt} = \frac{\Delta N_1}{\tau}$$

where τ is a reciprocal rate constant or relaxation time

and $$\frac{d(\bar{N}_1 + \Delta N_1)}{dt} = f_{o1}(\bar{N}_o - \Delta N_1) - f_{1o}(\bar{N}_1 + \Delta N_1)$$

i.e. $$\frac{1}{\tau} = f_{1o} + f_{o1}$$

If the perturbation is sinusoidal

$$\Delta N_1 = A \exp(iwt)$$

and the population at frequency w is increased by an amount ΔN_1^w which is less than ΔN_1, the increase in $\bar{N}_1$ at very low frequencies of perturbation. ΔN_1^w depends on the frequency w .
The difference $\Delta N_1 - \Delta N_1^w$ decreases with time:-

$$\frac{d(\Delta N_1 - \Delta N_1^w)}{dt} = \frac{\Delta N_1 - \Delta N_1^w}{\tau}$$

so that $$\frac{d\Delta N_1^w}{dt} = A \exp iwt/\tau$$

$$\Delta N_1^w = \frac{\Delta N_1}{1 + iw\tau}$$

This is directly related to the vibrational heat capacity since

$$C_{v1b}\Delta T = E\Delta N_1$$

thus $$C_1^w = C_1/(1+iw\tau)$$
$$= C_o - C_{oo}/(1+iw\tau)$$

therefore $$C_w = C_{oo} + (C_o - C_{oo})/(1+iw\tau)$$

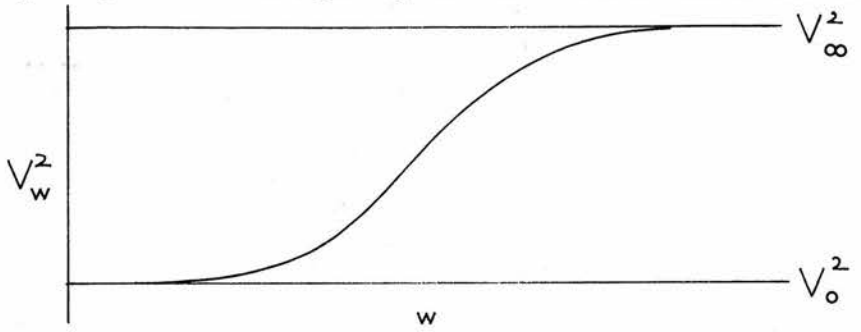
at frequency $$V_w^2 = \frac{RT}{M}\left(1 + R\,\frac{(C_o + C_{oo}w^2\tau^2)}{(C_o^2 + C_{oo}^2 w^2\tau^2)}\right) \quad (3)$$

when $w\tau << 1$ $$V_o^2 = \frac{RT}{M}(1 + R/C_o)$$

when $w\tau >> 1$ $$V_\infty^2 = \frac{RT}{M}(1 + R/C_{oo})$$

Under these two conditions, the velocity is independent of frequency, but at intermediate frequencies, equation (3) holds, and V_w^2 depends on frequency in the manner shown in Fig.1.

FIG 1



The inflexion point of the curve is at

$$W = \frac{1}{\tau} \quad \frac{Co}{Coo}$$

This relation has been found to hold for polyatomic molecules where there is more than one vibrational mode in extensive studies by Lambert and his co-workers (10). The explanation put forward is that energy equilibration occurs through the lowest mode, of specific heat C_1, and the other modes are closely coupled to it so that energy transfer between them is almost instantaneous. The relaxation time of this lowest mode is thus given by

$$\beta = \frac{\tau C_{1\,vib}}{\Sigma C_{vib}}$$

GAS MIXTURES.

The argument given above can be applied to binary mixtures, where more than one process contributes to the overall relaxation time $\bar{\tau}$. The total quantities for a mixture are related to the quantities for its individual components through their

mole fractions thus:-

$$\text{Co Mix} = X_A \, Co_A + (1 - X_A) \, Co_B$$

$$\text{Coo mix} = X_A Coo_A + (1 - X_A) \, Coo_B$$

$$B_M = X^2_A B_{AA} + 2X_A (1 - X_A) B_{AB} + (1 - X_A)^2 B_{BB}$$

where the subscripts refer to the two types of particle participating in the interaction. Three distinct types of interaction are involved in a binary mixture (11).
The relaxation equation is derived assuming that A is a two state vibrator as before, and that B has no vibrational energy.

$$\text{then} \quad \frac{dN_1}{dt} = (fo1^{AA} + fo1^{AB}) \, No - (f_1o^{AA} + f_1o^{AB}) N_1$$

from which it can be shown that

$$\frac{1}{\tau} = fo_1^{AA} + fo_1^{AB} + f_1o^{AA} + f_1o^{AB}$$

The two processes can be divided thus: Process AA occurs in the fraction $(1 - X_B)$ of the mixture, with a relaxation time τ_{AA}, so that

$$fo_1^{AA} + f_1o^{AA} = (1 - X_B) / \tau_{AA}$$

similarly

$$fo_1^{AB} + f_1o^{AB} = X_B / \tau_{AB}$$

finally

$$\frac{1}{\tau} = \frac{1 - X_B}{\tau_{AA}} + \frac{X_B}{\tau_{AB}}$$

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CHAPTER 3.

THE INTERFEROMETER.

In principle the ultrasonic interferometer consists of a source of ultrasound, a piezo-electric quartz crystal, and a moveable reflector between which standing waves are set up when their distance apart is an integral number of half-wavelengths. The problem of accurate interferometry lies in the accurate determination of the successive positions of the reflector which correspond to the establishment of standing waves in the interferometer tube. When a standing wave is set up, the initial pressure condensation from the transducer is exactly in phase with the pressure condensation of the reflected waves, and the excess pressure on the crystal is a maximum. At positions other than exact resonance, the pressure on the transducer is less, and the variation in pressure alters the impedance of the crystal and gas column, and thus changes the anode current in the oscillator. As the reflector passes through a resonance position, the anode current passes through a maximum giving rise to a resonance "peak". The accuracy of the measurement of the velocity of sound thus depends on the mechanical accuracy with which reflector movements can be measured, and the sharpness of the resonance peaks. Outside the dispersion region peaks are sharp because there is little dissipation of the energy emitted from the source, but in the dispersion region where time-dependent molecular processes absorb a considerable fraction of the sound energy, peaks are flatter and the problem of determining the maximum in a peak is great. The basic requirement is a large signal to noise ratio in the electronic circuitry, that is, a large rate of change of signal with reflector movement through the peak compared to the random rate of change of signal with time. Assuming that the electronic

circuitry is as stable as possible, the solution lies in finding a scanning speed for the reflector which produces sharp peaks without reducing the accuracy of the measurement of reflector travel.

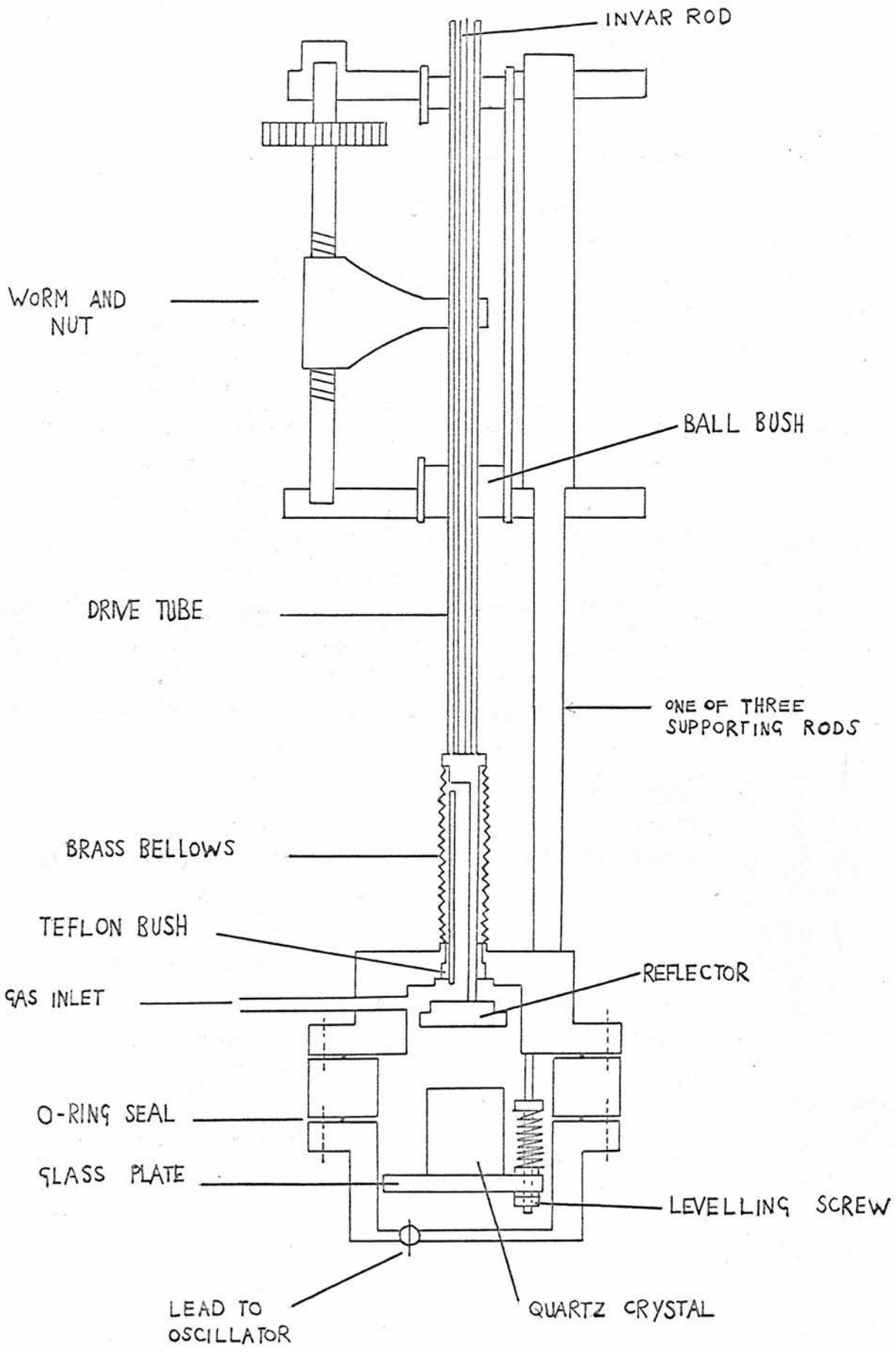


FIG. 2 THE INTERFEROMETER

THE PRESENT APPARATUS (FIGURE 2)

The interferometer pot is a stainless steel cylinder of 4 cm.internal diameter divided into three sections which are held together through rubber O-rings. The uppermost section is rigidly suspended from an inch-thick steel plate which is supported on two large concrete pillars to reduce vibration. Attached to this section are a gas inlet tap of the diaphragm type, and a set of bellows which allow the reflector to move 1.6 cm. in a vertical direction whilst maintaining the pot leak-tight. Three long screws are fixed vertically to the bottom of this section to provide a three-point adjustable mounting for the crystal, and each carries a nut which can be moved along the screw. "TEFLON" washers, backed by small adjusting nuts, support the glass plate upon which the crystal sits; the plate is held in tension by three springs which are compressed between it and the adjustable nuts. This arrangement provides a sensitive means of levelling the crystal. A collar and bottom plate, the latter fitted with a glass-metal seal for the electric connection to the crystal, make up the rest of the pot. The reflector, which has an optically flat reflecting surface, is driven by a synchronous electric motor running at 3 r.p.m. Between the motor and the final drive worm and nut gears is a brass gear box containing two ratios, direct drive and a 3 : 1 speed increase, which produce reflector speeds of 400 μ/minute and 1200 μ/minute. Reflector travel is sensed by an Invar rod to reduce thermal expansion effects, attached to the moveable head of a Moire fringe device made by Ferranti Ltd (12), which gives a digital read-out of the distance moved by the reflector with a least count of 1μtravel. Fractions of a micron can be interpolated on a small graduated oscilloscope.

The crystals were driven and positions of maximum acoustic impedance detected in two ways. Power at the

83kc/s crystal (0-4 volts) was supplied to a tank circuit from a variable frequency oscillator; the crystal was connected in parallel with the tank circuit and changes in crystal impedance observed by monitoring the crystal current. A standard crystal of similar frequency was used to measure the actual frequency of the crystal, the difference between the two being measured by the method of beats against a variable low frequency source. The 92.9, 93, 144, 152 kc/s crystals were used in the oscillatory circuit of a Colpitts oscillator, similar to that used by Matheson (13) at 10 volts at a frequency determined by a frequency meter. This arrangement produced better signals than the former and was used throughout the Co_2 - inert and methane work. The plate current was displayed on a chart recorder; alongside the main pen, a small pen attached to a solenoid produced a trace upon which a "blip" was impressed for every ten microns of reflector travel. Using the electrical frequency meter it was found that during the reaction time of the solenoid, the reflector moved 0.1 μ when running at 400 μ/minute, so that at 1200 μ /minute a "blip" is drawn within 0.3 μ of reflector travel from the nearest 'ten' position. The actual figures for the test are shown in Table I.

TABLE I

REACTION TIME OF SOLENOID	PULSE PERIOD at 400 μ/Min.	REACTION TIME OF SOLENOID
	1212 millisec	12.63 13.73 Av = 12.4 millisec 12.80 10.60

Power for the solenoid was taken from the "tens" circuit of the Ferranti counter, which produces a 15 volt pulse whenever this digit circuit changes. In this way, the actual position of a

resonance peak can be directly read off the chart; fluctuations in the speed of the chart motor can be neglected because, in effect a new reference point is impressed upon the chart for every ten microns of reflector travel.

The apparatus was set up as follows:-

A crystal of appropriate frequency was first tested on a bench using a variable frequency oscillator for suitable resonance responses, and was then placed in position suspended by the three screws, the two lower parts of the pot being set aside. Some crystals, particularly those in the 250-500 kc/s range possessed a set of closely spaced resonances; only one of these in general gave a strong response and produced measureable peaks in laboratory air. The optimum position for the crystal was judged to be that for which the main peak was most symmetrical and sharp, and the satellites (described later) smallest and least complicated in structure.

The following crystals were used:-

83 kc/s	Cylindrical, X-cut quartz, nodal mounting, gold surfaces with bevelled edges, and gold wires not directly attached to the sound emmitting surface.
92.89) 93.16) kc/s 144.5)	Cylindrical, X-cut, silvered surfaces, electrodes attached directly to the surface.
151.9 kc/s	Square, X-cut, gold surfaces; electrodes directly attached to the surfaces.

In lightly absorbing gases such as air and inerts, frequency changes were observed whenever a resonance position was traversed. The largest changes, of approximately 10 c/s occurred in air and depended on the roughly estimated activity of the crystal

ACCURACY OF THE INTERFEROMETER.

The arrangement should apparently be capable of a high degree of accuracy. Reflector travel can be measured on the Ferranti counter to 0.2 μ, and the frequency of the crystal can be measured to $\pm$ 1 c/s. Using a 100 kc/s. crystal, for which the wavelength of sound in air is approximately 3000 μ, the fractional errors in the measurement of wavelength and frequency are respectively 1 in 7000, and 1 in 100,000. In practice however the accuracy is greatly reduced because peaks are not infinitely sharp, and because the propagation characteristics of sound waves in the interferometer are not understood in exact detail.

The final error in the measurement of the plane-wave, ideal velocity of sound accumulates from two main operations, namely the location of individual peak positions, and the subsequent correction of the average wavelength to ideal conditions. Two sources of error are distinguishable in the location of individual peak positions, First, in dispersion regions where peaks are broad and small, quite large random variations in the position of the maximum in a peak can occur especially in mixtures with light molecules; in weakly absorbing gases this effect is not observed because the signal to noise ratio is more favourable. Secondly, the measurement of the maximum in a peak from the calibration "blips" is subject to inaccuracy. When making measurements in weakly absorbing gases, the reflector can be driven at 400 μ/min, due to the large and sharp resonance peaks produced, and the chart run at 4 inches per minute. Measurements in the dispersion region require a scan speed of 1200 μ/min, and the maximum chart speed of 8 inches/ min. The former combination necessarily gives a more accurate measure of the position of resonance peaks, and the latter combination represents a compromise; ideally a scan speed of 2400 μ/min should be used, but at this speed the "blips" which are printed out every 10 μ of travel

could not be distinguished on a chart running at 8 inches per minute. Using the first combination the position of a single peak can be measured to ± 1 μ whereas peaks in the dispersion region can be measured to ± 3 μ on the second combination. The standard deviation of any single measurement of peak position is approximately ± 5 μ; by scanning the peak many times a mean can be obtained with a standard deviation of approximately 1-3 μ., resulting in accuracies in λ means of the order of at least 1 in 1000.

SATELLITES.

Satellites affect the accuracy of peak location when they are large and unresolved from the main peak because they produce an unsymmetrical peak whose maximum cannot be geometrically located. In fact, since satellite separation increases with the ordinal number of the peak, geometrically located maxima will be separated by distances which increase with the ordinal number of the peak. The conditions under which the problem arises occur at high pressures and at frequencies where dispersion is slight. High densities favour the satellites and absorption is sufficient to broaden the main peak and so overlap it without eliminating it. Typical examples occur with CO_2 and neon, argon at f/p values of approximately 70 kc/s ATM. Satellites were most clearly seen in measurements in air or weakly absorbing gases as small subsidiary peaks, always placed on that side of the main peak which is more distant from the source; they were observed with each crystal, and could not be eliminated by careful levelling. The separation of main peak and satellite in all cases increased in an approximately linear manner with distance from the source, and increased as the wavelength of sound increased for the same crystal and different gases, and the same gas with different crystals. Satellite size varied from crystal to crystal, but was not related to the roughly estimated crystal activity; in all cases size decreased with distance from the source more rapidly than the

main peak, indicating that satellites are affected more strongly by absorption. Blythe (14) states that peak height is reduced by increasing the wavelength, and that satellites can be eliminated in this way, either by decreasing the frequency or changing to a gas with a longer wavelength. This is certainly true in the present apparatus when comparing gases such as air, argon or neon with helium, because helium produced symmetrical peaks without satellites, although at 93 kc/s slight asymmetry was detected. Kaye and Sherratt (15), from whom Blythe took his information, base their observations on hydrogen. However, frequency changes from 152 kc/s to 93 kc/s in air and inerts did not produce detectable diminutions in satellite activity, and only in certain cases did diminution occur for the same crystal in changing to gases with longer wavelengths. The data from which these conclusions are drawn are shown in Table (2). The source of the satellite effect is not known; a number of sources can be suggested, but the limited data available in the present work does not permit a firm statement to be made .

THE GRABAU EFFECT

When the position of each peak in a gas column has been located, successive $\lambda/2$ values can be calculated and an average λ value obtained; but even this apparently simple procedure can in some cases cause an error over and above that normally produced in the averaging of a normal distribution of results due to an effect first observed and studied by Grabau(16). The"Grabau" effect is the systematic variation in successive $\lambda/2$ values as the reflector moves away from the crystal, and was originally studied with a series of sources and reflector diameters. Grabau attributed the variations to diffraction effects set up when the diameter of the source and the wavelength were of similar magnitude. Only the 83 kc/s crystal, which was investigated by Blythe (14) showed a significant "Grabau" effect.

Typical runs in air are shown for the other crystals in Table(3), and exhibit a completely random distribution of successive half-wavelengths. However, there is some evidence that the Grabau effect depends on wavelength, that is, it becomes more pronounced as the wavelength approaches the diameter of the source. For example, at 92.89 kc/s, 144.5 kc/s and 152 kc/s no Grabau effect was observed in air, but wide variations of $\lambda/2$, not altogether reproducible, were observed in helium, Table (3). If a normal average λ is calculated from a series of successive $\lambda/2$ values in which Grabau variations are significant, then the accuracy to which this average can be quoted is less than the accuracy of an individual wavelength measurement, especially if a small number of peaks are available. For instance only three peaks were available in helium at 92.89 kc/s, and the average λ could only be quoted to 1%. However, by determining successive λ values from the formula

$$\lambda_{I,N} = \frac{X_N - X_I}{N - I}$$

where X_N, X_I are positions of the N^{th} and 1st peaks, the effect is reduced. One of the measuring techniques used for dispersing gases was to measure peaks 1, 4, 5 many times to obtain an accurate average peak position, and then calculate λ using the formula above. In order to ascertain whether this introduced a systematic error similar to the Grabau type, the following results were collected using a CO_2 - He mixture.

Run No.	1 - 4 μ	1 - 5 μ	1 - 7 μ	1 - 9 μ
1	1955.9	1955.4	1957.9	1957.1
2	1952.2	1952.5	1955.4	1954.4
3	1953.9	1957.1	1956.7	1955.6
Av.	1954.0	1955.0	1956.6	1955.7

The results show a random distribution of λ values from the peaks used and thus justify the procedure.

TABLE 2 SATELLITE DATA

Frequency Kc/s	Peak No.	ΔS Satellite Separation μ.	% Height	λ μ.	Gas
93	1	145	19	3740	Air
	2	175	19		
	3	215	14		
	4	230	16		
	5	280	15		
	6	280	14		
	7	300	13		
	1	85	63	2910	CO_2
	2	100	69		
	3	115	48		
	4	140	64		
144	1	90	18	2450	Air
	2	80	19		
	3	100	18		
	4	94	17		
	5	110	17		
	6	115	15		
	7	130	15		
	8	124	15		
	9	140	15		
	10	135	14		
	11	157	13		
	1	160	15	3160	Neon
	2	165	11		
	3	190	13		
	4	200	12		
	5	210	-		
	6	210	-		
152	1	80	33	2300	Air
	2	85	30		
	3	90	28		
	4	85	25		
	5	-	-		
	6	100	18		
92.89	1	112	40	3760	Air
	2	142	42		
	3	162	33		
	4	205	26		
	5	221	26		
	6	258	21		
	7	278	12		

TABLE 3.

SUCCESSIVE $\lambda/2$ VALUES. (μ.)

GAS	FREQUENCY. KC/S. 92.89		93.16		144.5				151.9	
	1	2	1	2	1	2			1	2
AIR	1890	1893	1886	1881	1210	1210			1153	1156
	1890	1883	1883	1886	1210	1210			1150	1150
	1882	1892	1884	1882	1212	1211			1154	1152
	1891	1889	1878	1884	1208	1211			1150	1149
	1886	1890	1886	1879	1212	1211			1151	1150
	1885	1889	1883	1887	1208	1211			1154	1152
	1890	1890	1880	1880	1211	1211			1152	1152
	1890	1891			1211	1210			1151	1148
					1213	1210			1148	1163
					1205	1212			1154	1155
					1203	1208			1152	1148
	= 3				1212	1213			1147	1152
	= .7				1212	1206			1155	1150
HELIUM	1				1	2	3	4	1	2
	5663		TWO		3584	3588	3585	3585	3413	3419
	5566		PEAKS		3566	3566	3565	3559	3391	3392
			ONLY		3607	3595	3610	3586	3417	3398
									3392	3408

THE TRANSVERSE WAVE EFFECT.

In all cases studied the final average λ value exceeded that calculated assuming that sound propagation occurs by plane waves. This is the "Transverse wave effect", so called because it is thought that propagation in a tube which is wider in diameter than the source of sound occurs by waves which are cylindrically symmetrical and have a particle velocity in a radial direction. Although many workers use velocity dispersion to measure relaxation times, few have actually observed the transverse wave effect because they calibrate their interferometers with air and inert gases. Stewart and Stewart (17) have observed the effect using a piston type interferometer at 4 Mc/s, and Blythe (14) studied the effect in the present apparatus at 83 kc/s; both found that the observed wavelength of ultrasound always exceeded the value calculated for plane waves by an amount proportional to the square of the wavelength. During the present investigation crystals of 92.9, 93.2, 144.5, 151.9 kc/s were used and the transverse wave correction studied with each one using inert gases and CO_2-free dry air. (Details of the purities of materials and the calculation of velocities of sound are to be found in the next chapter). The results are shown in Table (4), corrected to 30°C, and superimposed on the same graph in Fig (3). The relationship found empirically by Stewart and Stewart, and derived theoretically by Blythe is found to be obeyed approximately, although a positive intercept on the $\Delta\lambda/\lambda$ axis is indicated in some cases.

FIG: 3

THE TRANSVERSE WAVE CORRECTION

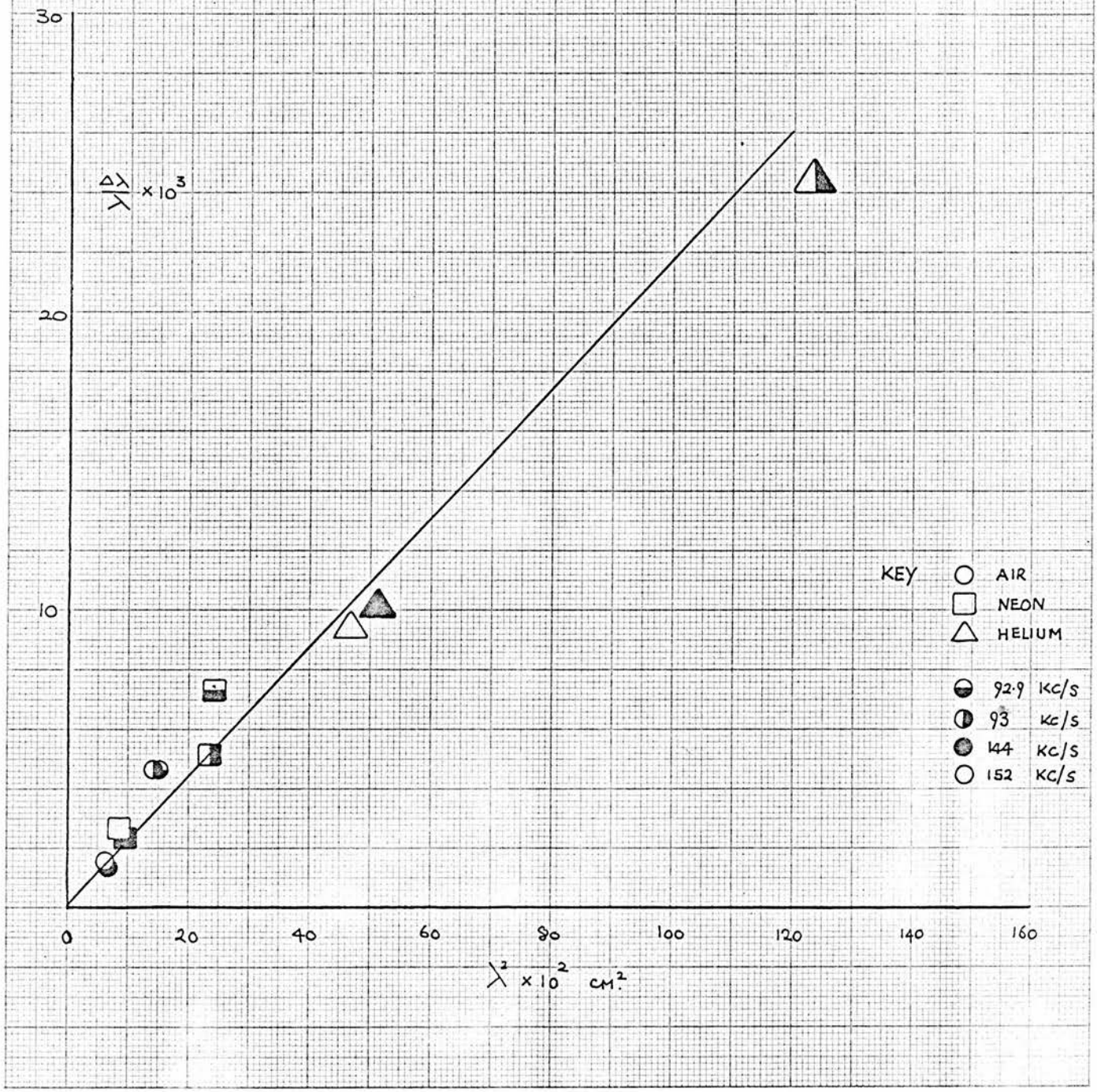


TABLE 4

TRANSVERSE WAVE CORRECTIONS 30°c.

Crystal Kc/s	Gas	Pressure cmHg	V Real Calc. cm/sec.	λ Real Microns	λobs. μ	Δλ	Δλ/λ X10³
92.89	Air	76	34926	3760	3777	17	4.4
	Neon ✱	15	45622	4912	4951	39	7.8
93.17	Air	183	34937	3749	3765	16	4.3
	Air	76	34931	3749	3765	16	4.3
	Neon ✱	39	45634	4898	4925	27	5.2
	Helium	54	102450	11001	11275	74	24.3
144.5	Air	74	34926	2417	2420	3	1.28
	Neon ✱	24	45629	3158	3165	7	2.25
	Helium	49	102478	7092	7164	72	10.1
151.9	Air	76	34931	2298	2302	4	1.74
	Neon ✱	49	45638	3004	3012	8	2.5
	Helium	41	102474	6744	6807	63	9.34

✱, The observed λ values in Neon are corrected for 0.1% helium.

It may be concluded that propagation in the interferometer is not by plane waves, but because the limiting velocities Vo and Voo for a dispersion region are calculated assuming plane waves, observed velocities must be corrected to the plane wave values by interpolation from the calibration graph; otherwise when two crystals are used to follow a dispersion region, there

will be a considerable mis-match at the f/p value where the change is made. The importance of the transverse wave effect for relaxation studies lies in the degree of uncertainty which interpolation produces from a graph for which only an empirical relation is known; the error involved is of the order of 0.03%. It is unlikely that the effect is due solely to the design of the present interferometer pot, because further evidence is available from a number of sources using apparatus of different dimensions. Matheson found a transverse wave effect, different in magnitude from the present results, in an interferometer of 10 cm. internal diameter with 83,227 and 694 kc/s crystals, and Stewart and Stewart used a piston type interferometer at approximately 4 Mc/s. As early as 1934, Eucken (18) was calibrating his apparatus for an effect similar to the transverse wave effect.

THE VIRIAL CORRECTION .

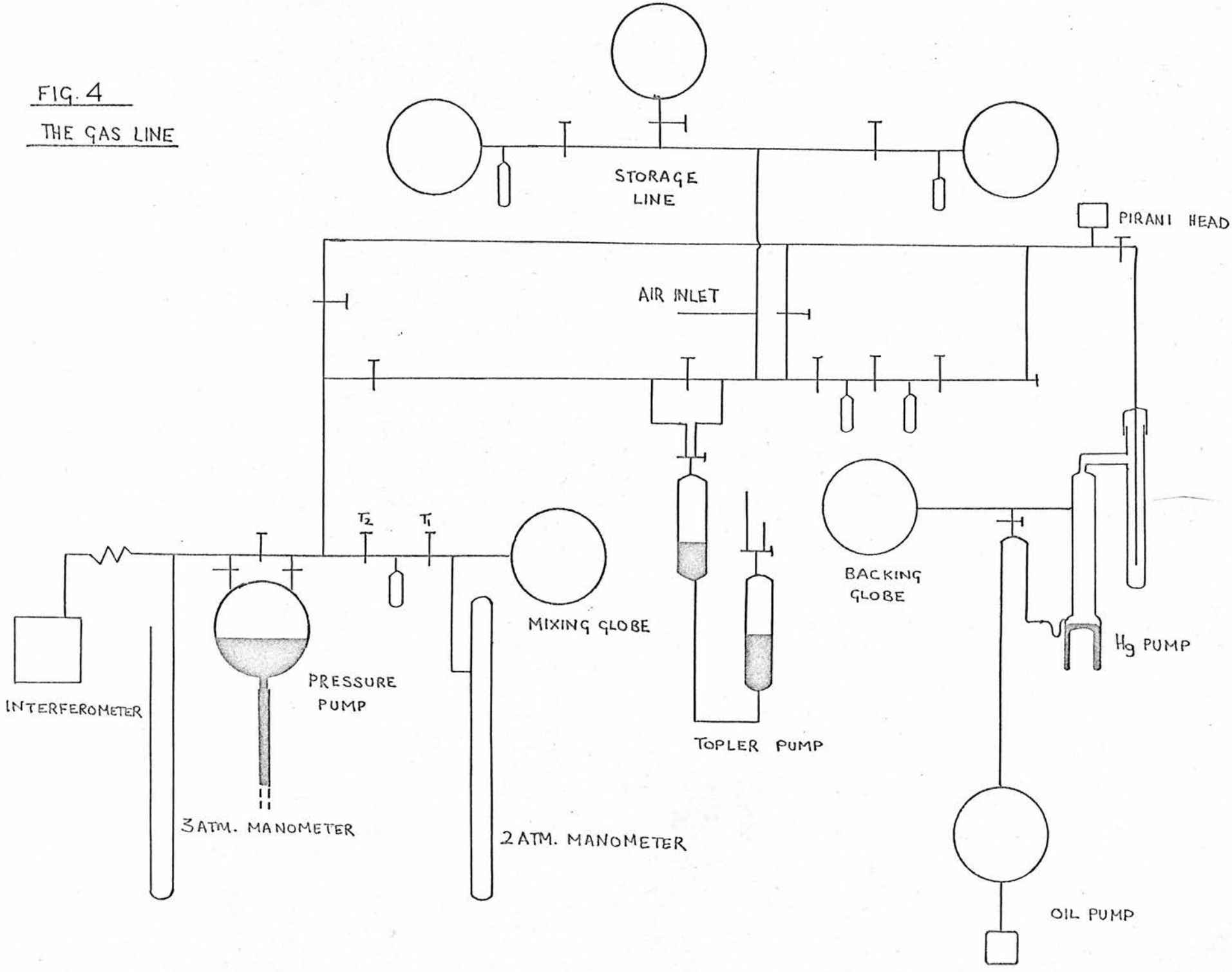
The final source of error arises from the necessity to express velocities of sound for dispersion studies as ideal gas velocities. In plotting V_w^2 against log f/p and varying the pressure at constant frequency, it is assumed that a two-fold increase in pressure is exactly equivalent to a two-fold decrease in frequency, and this is only exactly true for an ideal gas. Now since the upper part of the dispersion curve is examined in all but one of the dispersion studies undertaken in the present work, the largest error due to velocity correction will in general be at the point furthest into the region because the velocity correction is proportional to pressure, and measurements at V_∞^2 will incur a negligible error. However the maximum error is not greater than 1 in 2000.

Thus apart from the transverse wave correction all the errors in the present dispersion studies are greatest at the point furthest into the dispersion region. However, as the theoretical dispersion curves tend to cluster as they approach the limit V_∞^2

and are most widely separated at the inflexion point, the accuracy with which a relaxation curve is defined remains fairly constant throughout the region studied. Moreover this degree of accuracy remains fairly constant over a wide range of conditions due to the compensation of various effects. Thus the accuracy with which V_∞^2 is defined depends on two factors: at V_∞^2 only classical absorption is involved, so that resonance peaks should be sharp, but V_∞^2 is measured at high f/p values, that is, at low pressures where gas density is low, so that the acoustic impedance is also low and peaks decrease in size accordingly. Similarly, the accuracy with which peak positions can be measured in methane is far greater than that in CO_2 because the relaxing specific heat is smaller, but this also means that the dispersion curves in CH_4 are flatter and cluster together more.

FIG. 4

THE GAS LINE



THE GAS-HANDLING SYSTEM.

A schematic diagram of the interferometer and gas handling system is shown in Fig (4). The pumping system consists of a glass, mercury diffusion pump backed by a rotary oil pump. Between the pump and the vacuum line is a liquid nitrogen trap which prevents mercury passing into the apparatus and protects the oil pump from harmful condensible vapours. The vacuum line is attached to the interferometer through a glass metal seal which is protected from strain by a glass spiral. Attached to the line are gas storage globes with freeze-out traps, a 2-atmosphere mercury manometer and several subsidiary manometers, a Töpler pump and an air purification train. A metal grid supports the line, which is divided into sections by ground glass taps lubricated by Apiezon L grease. The mixing globe consists of a detachable 1 litre "Quickfit" globe to which is attached a 2-atmosphere mercury U-tube manometer. The globe feeds into the vacuum line through two taps, between which is a small cold trap; it can be supplied with non-condensible gases using the Töpler pump.

Mixtures were made up as follows:- Carbon dioxide was passed into the evacuated globe previously lined with P205 as a drying agent, to the required pressure, and then frozen out into a nearby cold trap. The non-condensible gas was then let into the globe to the required pressure, and tap T_1 closed. After evacuating the line, the CO_2 was frozen into the small cold trap, T_2 closed and T_1 opened. The gases were allowed to warm up to room temperature to mix for 48 hours. For total mixtures pressures above 1 atmosphere, taps were retained by stout rubber bands and the globe held in position by two springs.

In order to measure velocities of sound at 40 kc/s.atm, pressures up to 2.4 atmospheres were employed. A modified Töpler pump of 600 cc. capacity was constructed of pyrex glass with spring-loaded ground glass taps to withstand the high pressures; these latter were achieved by using a mercury reservoir connected to the

pump which could be elevated to a height of 100 cm. above the pump chamber. The pressure was measured in an open-ended 2-atmosphere manometer. At 3 atmospheres pressure the separation of the mercury levels in the limbs is only 152 cm. The pump itself is so placed that the reservoir can be 76 cm. below it for high vacuum pumping, and 100 cm. above it for pressure pumping. The two extreme positions do not require the same amount of mercury, so a pump was installed to draw off mercury in the high vacuum position. This aleviates strain in the reservoir and ensures that in the 1-atmosphere position only a small part of the pump contains mercury, and thus the maximum compression ratio is obtained. The complete apparatus is housed in a basement room well insulated from vibration in the building, and is thermostatted at $21 \pm .02^{\circ}C$. The interferometer itself is thermostatted at $30 \pm 0.02^{\circ}C$ in a silicone oil bath.

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CHAPTER 4.

M A T E R I A L S.

The following gases were used in the determination of transverse wave corrections:- Air, Helium, Neon, Argon.

AIR

Air was rendered dry and free from CO_2 by passing it slowly through caustic soda solution, conc. H_2SO_4, fused $CaCl_2$, "SOFNOLITE" and P_2O_5 dispersed on glass wool. The theoretical ideal velocity of sound was calculated from the equation.

$$V^2 = RT/M \ (1 + C_v /R)$$

assuming that at 100 kc/s atm. the vibrational specific heat contribution is absent, as shown by Knoetzel (19).

At 303°K, $V = 349.21 \pm 0.17$ m/s;

The error of 1 in 2000 is produced by the day to day variation in the density of the atmosphere. Virial data from Holborn and Otto (20) were used, B' and B" being derived graphically from the temperature dependence of B. This procedure introduces a negligible error.

INERT GASES.

Ideal velocities of sound in inert gases were calculated assuming a specific heat contribution from three translational degrees of freedom. The impurities in the inert gases, supplied by B.O.C. Ltd., were:

He	100%	He ;	2 v.p.m. CO_2 ;	4 v.p.m. O_2	
Ne	99.9%	Ne ;	0.1% He ;	2 v.p.m. O_2;	1 v.p.m H_2
Ar	100%	Ar ;	1 v.p.m. CO_2 ;	2 v.p.m. O_2.	
Xe	99%	Xe ;	Balance Kr.		

Errors due to uncertainties in atomic weights are negligible, and the

calculated values of sound velocities at 303°K, are reported in Table (5) without error limits. Virial data were taken from the following source, using the procedure as described for air.

He, Ne, Ar - Holborn and Otto (20)

Table VELOCITY DATA FOR AIR AND INERT GASES

Gas	V.ideal cm/sec.	S $cm^3 mole^{-1}$	V Real (1atm.) cm/sec.
He	102,450	+ 11	102,494
Ne	45,620	+ 12	45,644
Ar	32,430	+ 1	32,431
AIR Voo	34,921 ± 17	+ 8	34,931 ± 17

The following gases were used for relaxation studies:-

CO_2 ; He, D_2, Ne, Ar, Xe.

CH_4 ; He, D_2, O_2.

CARBON DIOXIDE.

This was prepared by the thermal decomposition of $NaHCO_3$ in vacuo, was dried over $CaCl_2$ and P_2O_5 dispersed on glass wool, and was finally degassed in liquid nitrogen for twelve hours and stored over P_2O_5. Mass spectrometer and infra-red analyses showed no detectable impurities. Samples were never allowed to remain in the interferometer for long periods, because experiments showed that quantities of water vapour sufficient to affect the velocity of sound in CO_2 were desorbed from the walls of the vessel over a period of twelve hours. Many workers, including Pielemeier (21) have observed the profound effect of water vapour on relaxation in CO_2.

Spectroscopic data for the calculation of the vibrational specific heat of CO_2 were obtained from Herzberg (22), who gave the following assignments.

ν_1 1285.5 cm^{-1}, 1388.3 cm^{-1} } Raman $C_{vib} = 0.073$ R

ν_2 667.3 cm^{-1} X.2 $C_{vib} = 0.461$ R

ν_3 2349.3 cm^{-1}

The vibrational specific heat is given by the Einstein equation:-

$$C_{VIB} = R \sum (h\nu/kT)^2 \frac{\exp(h\nu/kT)}{(\exp(h\nu/kT)-1)^2}$$

V_o and V_{oo} were calculated assuming that the total vibrational specific heat relaxes through the 667 cm^{-1} mode, so that V_{oo} corresponds to translational and rotational contributions only. Virial data were obtained from three sources, Michels & Michels (23), McCormack and Schneider (24), and Cottrell and Hamilton (25) and the factors B', B" obtained (a) graphically, (b) from an analytical expression given by the second authors, and (c) from tables supplied in Hirschfelder, Curtiss and Bird (11) assuming a Lennard-Jones potential. The three sets of values are compared in Table (6) T= 303°K ; those of McCormack and Schneider were used, but account was taken of the other two methods in the error limits of the velocity correction at 1 atm pressure(Table 6).

TABLE 6

METHOD	B	TB'/C	$T^2B''/2c(c+1)$	S	Vid	ΔV	Vreal
	cm^{3}mole^{-1}				cm/sec.		
Graphical	-119	+ 108	-60	-60	Vo27140		
Analytical	-121	+116	-50	-55	V_∞ 28320	-63	28257 ± 10
L - J	-120	+101	-34	-53			

DEUTERIUM.

This was drawn from a Matheson Co.Ltd., lecture bottle and used without further purification other than drying over P_2O_5. Mass spectrametric analyses showed no impurities in the mass range 10-40. The specific heat was calculated assuming that the rotational modes are still in equilibrium with translation at 100 kc/s.atm., according to Stewart and Stewart (26), whilst the vibrational contribution was neglected. For the 98 -2 CO_2-D_2 mixture, virial data for CO_2 were used, but for the 92-8 mixture, L-J data were derived (11).

VIRIAL DATA FOR MIXTURES.

Table (7) indicates the method used and the results obtained at 303°K. in deriving virial data. Two combining rules were used.

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2$$
$$\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}$$

TABLE 7

Method	Mixture	B_{AA}	B_{AB}	B_{BB}	B_M	$TB'm/c$	$T^2B''m/2c(c+1)$	S
				cm^3mole^{-1}				
Analytical								
	CO_2D_2 98/2	-121			-116			-53
L - J	92/8	-120	+8	+14	-102	+64	-18	-56
Graphical( )								
	CO_2He 9/1	-119	+21	+12	-92	+99	-59	-52
L - J	CO_2Ne 1/1	-120	+4	+11	-25	+37	-12	o
	6/4				-30	+59	-24	+5
L - J	CO_2Ar 6/4	-120	-49	-15	-69	+76	-28	-21
	8/2				-91	+88	-31	-34
L - J	CO_2Xe 1/1	-120	-121	-120	-121	+121	-50	-50

METHANE.

This was drawn from a cylinder (95%), trapped into liquid nitrogen, and the top fraction pumped away. The remainder was then distilled on the Clusius-Riccobini column (27), producing samples which contained, by mass spectrum analysis, 0.3% of other hydrocarbons, and was finally stored over P_2O_5. The following spectral assignments were given by Herzberg (22).

ν_4	1306 cm^{-1}	X3	Cvib = 0.235R
ν_2	1520 cm^{-1}	X2	Cvib = 0.077R
ν_1	2914 cm^{-1}		
ν_3	3020 cm^{-1}		

It was assumed that the total vibrational specific heat relaxes through the 1306 cm^{-1} mode. Virial data were calculated from Lennard-Jones parameters and are shown in Table 8 for T=303°K.

TABLE 8.

B	TB'/C	$T^2B''/2c\ (c+1)$	S	Vid	$\triangle V$	V real
$cm^3\ mole^{-1}$				cm/sec.		
-41	+37	-11	-15	Vo45233	-28	45205
				Voo45769		45741

OXYGEN.

This was drawn from a cylinder whose stated purity (99.5%) was confirmed by ultrasonic velocity measurement and was dried over P_2O_5. Virial data at 303°K for this and other mixtures were calculated from Lennard-Jones parameters, as shown in Table (9).

TABLE 9

Method	Gas	B_{AA}	B_{AB}	B_{BB}	Bm	TB'm/c	$T^2B''/2c(c+1)$	S
				$cm^3 mole^{-1}$				
L - J	CH_4O_2 1/1	-41	-27	-16	-27	+32	-10	-5
L - J	CH_4He 8/2	-41	+18	+9	-19	+26	-8	-1
L - J	CH_4D_2 8/2	-41	+8	+14	-22	+27	-8	-3

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CHAPTER 5.

R E S U L T S.

CARBON DIOXIDE AND MIXTURES, 303°K.

The work on CO_2 and additives can be divided into two parts.

a) low pressure work, $<$ 100 cm pressure, for mixtures giving relaxation times of less than 4 μsecs. A lower f/p limit of 130 kc/s.atm. was found satisfactory for defining relaxation times of this order or less.

b) high pressure work for mixtures with overall relaxation times greater than 4 μsecs, where a minimum f/p of 47 kc/s.atm. was found adequate.

In part (a) non-recoverable mixtures with helium and deuterium were made up to 100 cm. pressure in the mixing globe. The mixture was equilibrated with the pot and then progressively let out so that the first measurements were obtained at a pressure of 85 cm. mercury, the second at 65 cm. and so on. A number of runs were carried out in the region of 400 kc/s.atm. to define V_∞ accurately. Mixtures were allowed to warm up for not less than one hour in the interferometer before measurements were commenced. The technique of measurement consisted of running the reflector at one of the combinations described on page 20 , and switching on the solenoid on the count of an "100" approximately 200 μ. before the peak was expected. The frequency of the crystal was monitored continuously throughout a run, of which six or more were made depending on the number of peaks available. On the average, seven or eight peaks were available throughout the entire reflector travel, although in CO_2-He and CO_2-D_2 mixtures only five peaks were measureable. No run was carried out if the degassing rate of the interferometer was greater than 6 microns Hg.in one hour.

The final choice of mixture composition was made after preliminary experiments had given an indication of the relaxation time of the mixture. Reference to the equation relating the overall relaxation time τ to the mole fractions of the components and their individual relaxation times τ_{AA}, τ_{AB}.

$$\frac{1}{\tau} = \frac{1 - X_B}{\tau_{AA}} + \frac{X_B}{\tau_{AB}}$$

shows that the two quantities on the right hand side of the equation should be at least of the same order of magnitude if X_B/τ_{AB} is to be defined accurately. For CO_2He, a 9/1 mixture was used, and for CO_2D_2 a 98/2 mixture, since deuterium was found to be four times as efficient as helium in de-exciting CO_2. In part (b) a compromise had to be made in the choice of optimum composition. For components less efficient than pure CO_2, the mole fraction should be as large as possible, but as X_B increases, the amount of the dispersion region available to the present apparatus decreases and the accuracy to which $1/\tau$ can be measured is reduced. In order to recheck the consistency of composition through a series of runs, V_{∞} results were also taken from samples used for high pressure runs; in all cases they agreed with values obtained with fresh low pressure samples. In runs for which high pressure pumping was available, it was possible to retrace, using a new sample, part of the dispersion curve defined with the first sample. This provided a check on the significance of the variation of V_{ω}^2 with f/p. In all cases the observed V_{∞}^2 values agreed with those calculated from a knowledge of the partial pressures of individual gases used to make up the mixtures. The results in the following table have been corrected to 303°K, and the reported wavelengths λ corrected for the transverse wave effect. Error limits

have not been included in the tables, but arise in the following manner, taking CO_2 as an example.

	% error in λ mean	= 0.05	
	% error in λ with TWC	= 0.08	= % error in Vobs.
	% error in V ideal	= 0.12	
therefore	% error in V^2	= 0.24	
		= $\pm$ 0.02 x 10^8 $(cm/sec)^2$	

The errors in τ values were determined by inspection of the fit of individual points to a set of theoretical dispersion curves.

SECTION A .

1. CARBON DIOXIDE.

Three crystals were used to define the relaxation time of pure CO_2, and agreement between the sets of results is good. All are collected in tables 10, and 11, including one result at 93 kc/s; they were analysed assuming a single relaxation process, and are shown in Fig (5).

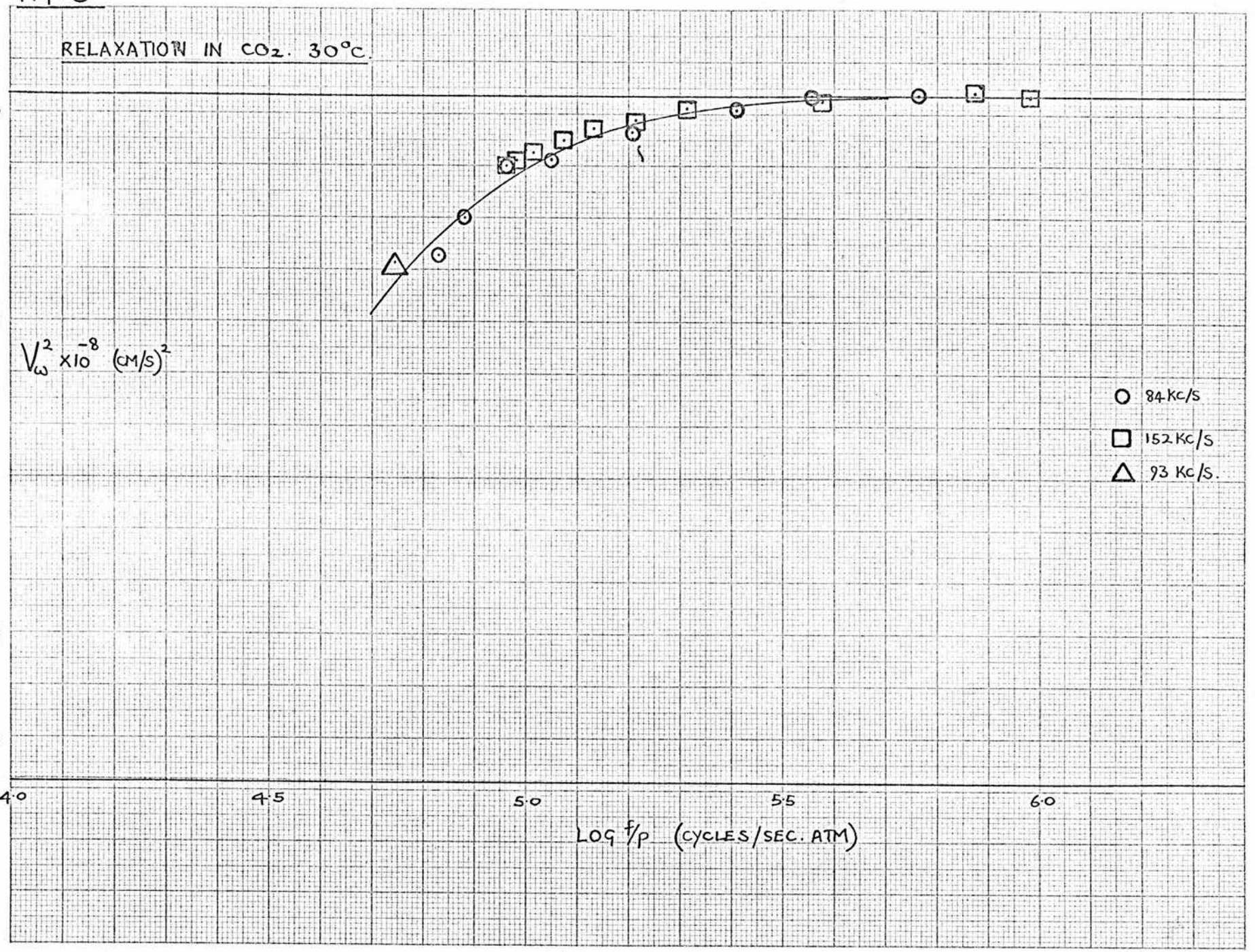
SET "A"

FREQUENCY = 83,870 c/s VOLTAGE = 10 SENSITIVITY (0-1)= 1
SCAN SPEED = 400 μ/min CHART SPEED = NIL. TWC = 8μ.

TABLE 10.

P cm.Hg.	λ microns	V ideal cm/sec.	V^2 X10^{-8} $(cm/sec)^2$	log f/p
92	3338.2	28050	7.86_8	4.838
82	3346.2	28108	7.90_1	4.886
71	3357.5	28193	7.94_8	4.959
56	3361.0	28206	7.95_6	5.052
40	3368.3	28256	7.98_4	5.205
25	3374.4	28294	8.00_6	5.402
17	3378.1	28318	8.01_9	5.554
11	3378.4	28315	8.01_7	5.757

FIG: 5


RELAXATION IN CO_2. 30°C.
8·0
7·9
7·8
7·7
7·6
7·5
7·4
7·3
$V_\omega^2 \times 10^{-8}$ (CM/S)^2
84 Kc/s
152 Kc/s
93 Kc/s.
4·0
4·5
5·0
5·5
6·0
LOG f/p (CYCLES/SEC. ATM)

SET "B"

FREQUENCY = 151, 920 c/s VOLTAGE = 10 SENSITIVITY = 0.5
SCAN SPEED= 1200 μ/Min. CHART SPEED = 8"/Min. TWC =1.5μ

With the exception of CO_2 Set "A", and CO_2Xe, which were measured with a scan speed of 400μ/min, all CO_2 and mixture results were carried out with a 1200μ/min scan speed and 8"/min chart speed, and with crystal voltage of 10V.

TABLE 11.

P cm.Hg	λ microns	V ideal cm/sec.	V^2 X 10^{-8} $(cm/sec)^2$	log f/p
125	1848.9	28195	7.95_0	4.97
119	1850.1	28208	7.95_7	4.99
113	1851.2	28220	7.96_4	5.01
95	1853.5	28239	7.97_5	5.08
83	1855.7	28261	7.98_7	5.14
70	1857.6	28279	7.99_7	5.22
56	1860.0	28303	8.01_1	5.31
30	1861.9	28309	8.01_4	5.58
15	1863.5	28320	8.02_1	5.89
11	1863.1	28312	8.01_9	6.02
FREQUENCY = 93, 170 c/s			TWC = 10 μ.	
128	2997	28040	7.86_2	4.74

The overall result for the three sets of data is

τ = 6.8 $\pm$ 0.3 μsec at 303°K, 1 atmosphere pressure.

SECTION A.

2. CARBON DIOXIDE - HELIUM.

Three distinct 9/1 mixtures were measured at 152 kc/s. The results are tabulated in Tables 12, 13 and 14, and displayed on a standard graph in Fig 6. This was achieved by calculating the Υ value for each individual point and re-deriving V_∞^2 with respect to standardised values of Vo and Voo.

SET A.

FREQUENCY = 151,920 c/s TWC = 1.9 μ

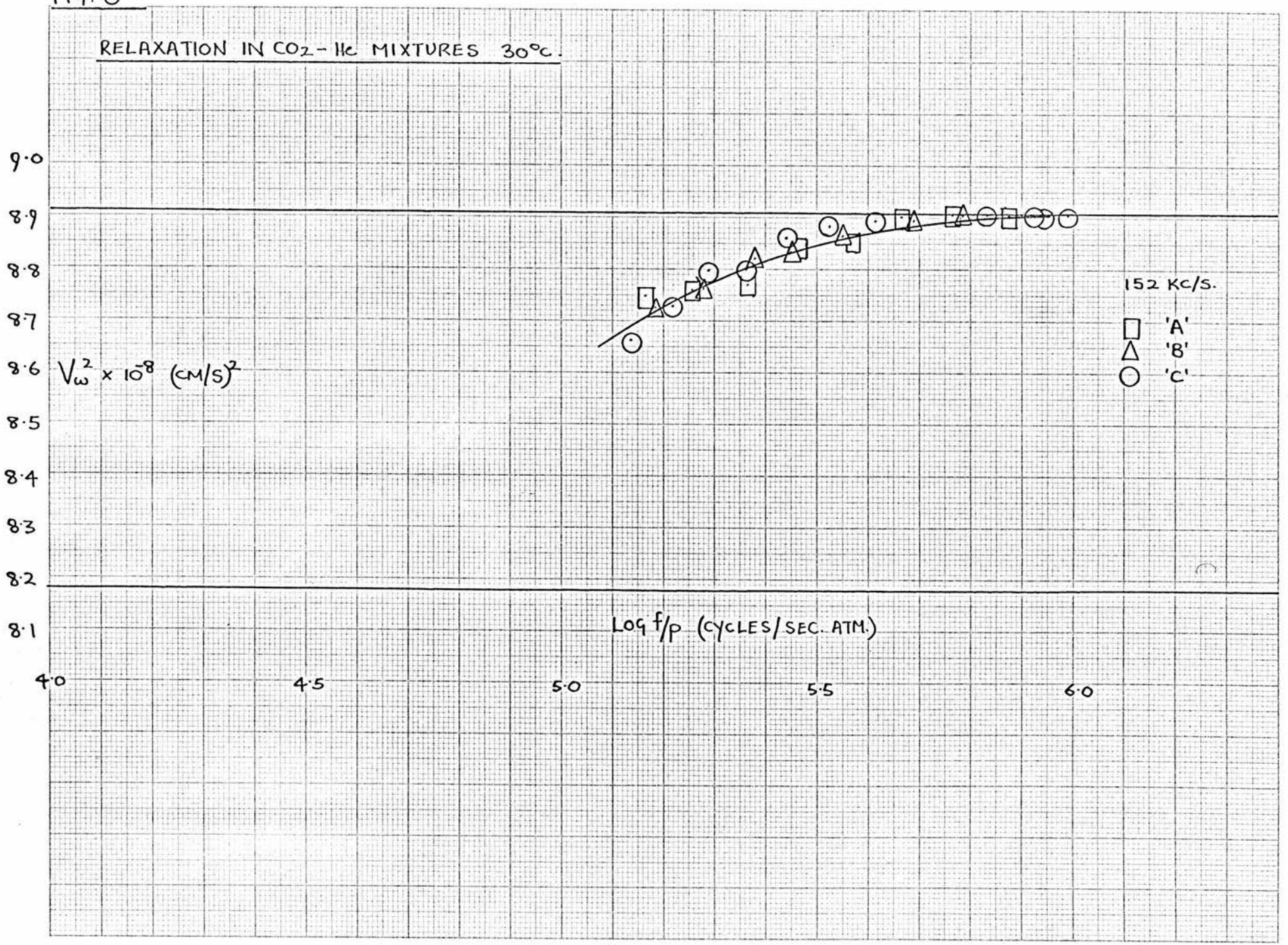
COMPOSITION: 91.9% CO_2; $Vo^2 = 8.02_7 \times 10^8 (cm/sec)^2$

8.1% He ; $Voo^2 = 8.75_0 \times 10^8 (cm/sec)^2$

TABLE 12.

P cm.Hg	microns λ	V Ideal (cm/sec)	V^2 x 10^{-8} $(cm/sec)^2$	log f/p
80	1926.8	29331	8.59_3	5.159
63	1929.0	29350	8.62_0	5.263
50	1931.9	29396	8.64_0	5.363
39	1937.8	29474	8.69_0	5.467
32	1940.1	29501	8.70_0	5.557
25	1945.4	29575	8.74_9	5.664
20	1946.5	29587	8.75_6	5.761
15	1946.4	29583	8.75_0	5.875

FIG: 6


RELAXATION IN CO2 - He MIXTURES 30°C.
9·0
8·9
8·8
8·7
8·6
8·5
8·4
8·3
8·2
8·1
$V_\omega^2 \times 10^{-8}$ (CM/S)²
152 Kc/S.
'A'
'B'
'C'
Log f/p (CYCLES/SEC. ATM.)
4·0
4·5
5·0
5·5
6·0

SET B.

COMPOSITION : CO_2 = 90.5% $Vo^2 = 8.15_7 \times 10^8 (cm/sec)^2$

He = 9.5% $Voo^2 = 8.87_1 \times 10^8 (cm/sec)^2$

TABLE 13

P cm.Hg	λ microns	V ideal (cm/sec)	V^2 X 10^{-8} $(cm/sec)^2$	log f/p
77	1937.7	29494	8.70_0	5.174
61	1943.5	29570	8.74_0	5.275
48	1948.9	29642	8.78_0	5.377
38	1950.9	29664	8.80_0	5.463
32	1956.0	29737	8.83_4	5.553
24	1958.9	29775	8.87_0	5.682
19	1958.9	29771	8.86_3	5.784
15	1960.8	29796	8.87_8	5.886

SET C.

COMPOSITION: CO_2 = 90.2% $Vo^2 = 8.18_1 \times 10^8 (cm/sec)^2$

He = 9.8% $Voo^2 = 8.90_6 \times 10^8 (cm/sec)^2$

TABLE 14.

P cm.Hg	λ microns	V ideal (cm/sec)	V^2 X 10^{-8} $(cm/sec)^2$	log f/p
84	1934.7	29453	8.67_2	5.138
71	1942.0	29557	8.74_0	5.210
59	1949.8	29664	8.80_0	5.290
49	1950.8	29672	8.80_4	5.367
42	1958.3	29780	8.86_8	5.444
35	1960.6	29809	8.88_6	5.522
14	1963.9	29843	8.90_6	5.929

Analysed individually, the three sets of data gave the following overall relaxation times, assuming single dispersion:-

A : τ overall = 3.0 ± 0.3 μsec

$\therefore$ τ CO_2He = 0.41 ± 0.1 μsec

B : τ overall = 2.6 ± 0.1 μsec

$\therefore$ τ CO_2He = 0.38 ± 0.5 μsec

C : τ overall = 2.5 ± 0.1 μsec

$\therefore$ τ CO_2He = 0.36 ± 0.05 μsec

the error limits on τ CO_2He include a 5% error in Co_2.

The final value is thus:-

τ CO_2He = 0.38 ± .04 μsec. at 303°K, 1 atmosphere pressure.

SECTION A.

3. CARBON DIOXIDE - DEUTERIUM.

Two distinct 98/2 mixtures were measured at 152 and 93 kc/s respectively. The results are shown in Tables 15 and 16, with separately derived τ values, and displayed on a standard graph in Fig (7) .

SET A.

FREQUENCY = 151,920 kc/s. TWC = 1.7 μ.

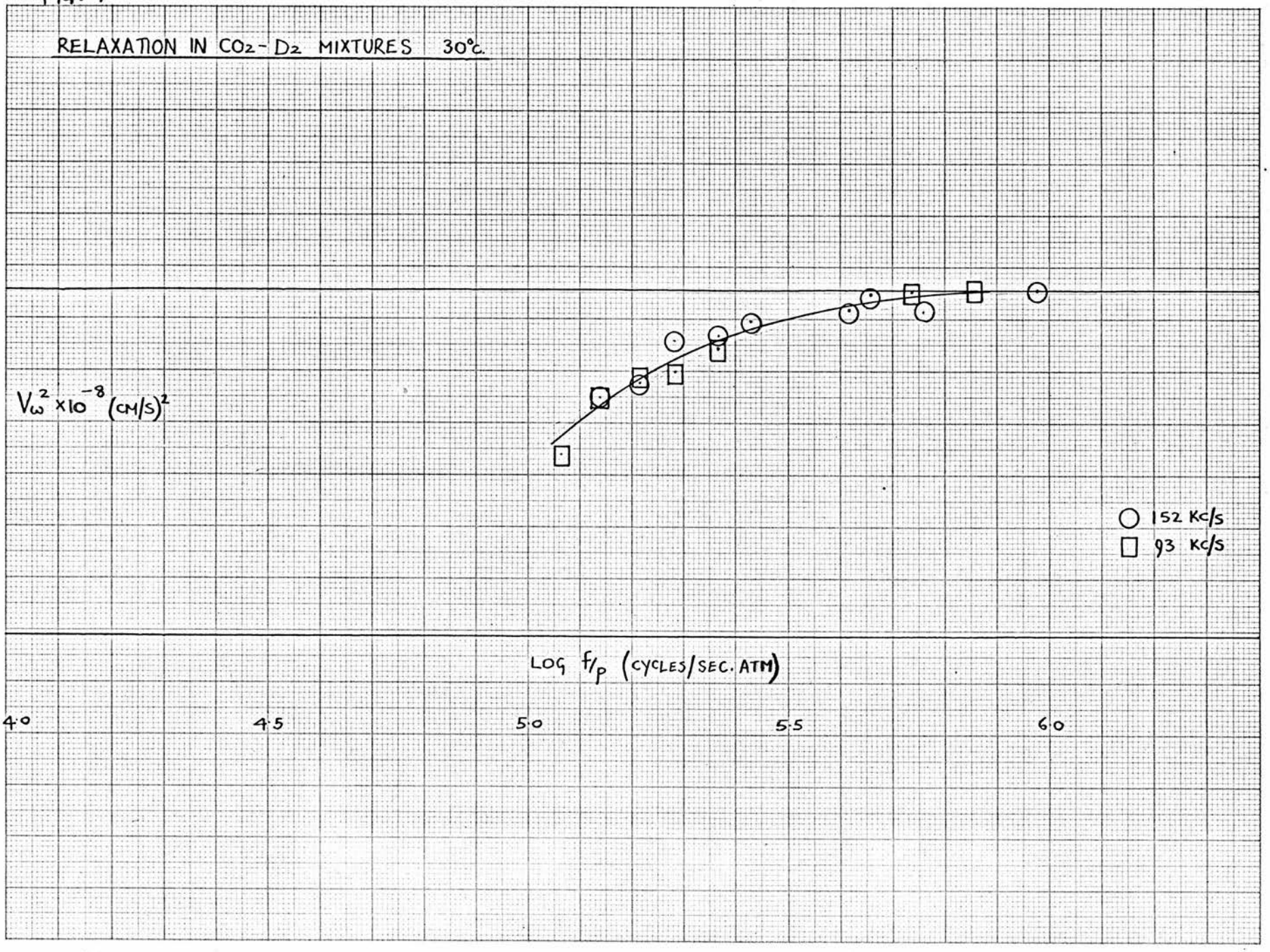
COMPOSITION: CO_2 = 98.1% $Vo^2 = 7.49_2 \times 10^8 (cm/sec)^2$

D2 = 1.9% $Voo^2 = 8.15_5 \times 10^8 (cm/sec)^2$

TABLE 15

P cm.Hg	λ microns	V ideal (cm/sec)	$V^2 \times 10^{-8}$ $(cm/sec)^2$	log f/p
85	1851.7	28204	7.97_0	5.137
71	1855.2	28246	7.98_0	5.212
60	1865.5	28394	8.06	5.282
50	1867.5	28416	8.07	5.367
42	1869.8	28446	8.10_0	5.443
35	1878.9	28578	8.17_3	5.521
28	1874.8	28511	8.13_3	5.615
24	1877.0	28535	8.15_0	5.677
20	1874.2	28496	8.12_4	5.755
12	1878.0	28553	8.15_9	5.982

FIG: 7


RELAXATION IN CO2 - D2 MIXTURES 30°C.
8·3
8·2
8·1
8·0
7·9
7·8
7·7
7·6
7·5
7·4
Vω² x10⁻⁸ (CM/S)²
LOG f/p (CYCLES/SEC. ATM)
4·0
4·5
5·0
5·5
6·0
152 Kc/s
93 Kc/s

SET B

FREQUENCY = 93.170 c/s TWC = 10 μ

COMPOSITION CO_2 = 98.5% $Vo^2 = 7.46_3 \times 10^8 (cm/sec)^2$

D 2 = 1.5% $Voo^2 = 8.12_5 \times 10^8 (cm/sec)^2$

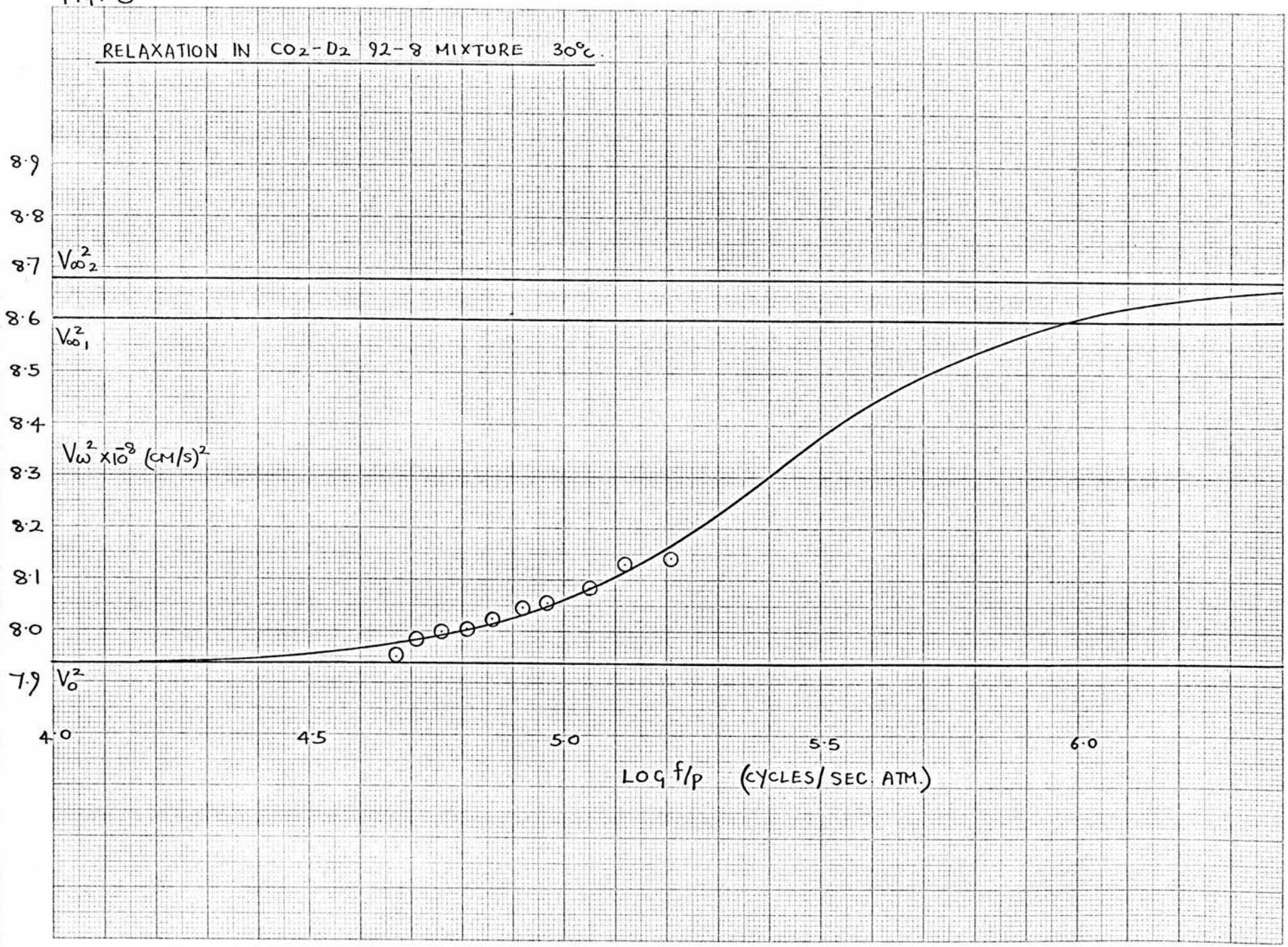
TABLE 16

P cm.Hg	λ microns	V ideal (cm/sec)	$V^2 \times 10^{-8}$ $(cm/sec)^2$	log f/p
61	3007.3	28063	7.87_5	5.067
51	3021.0	28182	7.94_2	5.142
43	3030.0	28260	7.99_0	5.216
36	3030.0	28254	7.98_3	5.294
31	3040.1	28343	8.03_3	5.362
13	3057.0	28488	8.12_0	5.726
10	3058.9	28511	8.12_9	5.85
8	3056.0	28474	8.11_0	5.947

The combined results produce the following result:-

τ CO_2-D_2 = 0.071 $\pm$ .01 μsec. at 303° K and 1 atmosphere pressure

FIG: 8


RELAXATION IN CO_2-D_2 92-8 MIXTURE 30°C.
8·9
8·8
$V_{\infty_2}^2$
8·7
8·6
$V_{\infty_1}^2$
8·5
8·4
$V_\omega^2 \times 10^{-8}$ (CM/S)^2
8·3
8·2
8·1
8·0
7·9
V_0^2
4·0
4·5
5·0
5·5
6·0
LOG f/p (CYCLES/SEC. ATM.)

SET C.

One mixture with the composition 92 - 8 CO_2 - D_2 was made up and measured using the 92.89 kc/s crystal. The results are shown in Table 17 and are displayed on Fig (8).

FREQUENCY = 92,890 c/s TWC = 9 μ.

COMPOSITION: CO_2 = 92.5% $Vo^2 = 7.93_1 X\ 10^8 (cm/sec)^2$

D2 = 7.5% $Voo_1^2 = 8.60_8 X\ 10^8 (cm/sec)^2$

$Voo_2^2 = 8.68_1 x\ 10^8 (cm/sec)^2$

Voo_1^2 corresponds to the presence of the rotational modes of deuterium and the absence of the vibrational modes of CO_2. Voo_2^2 corresponds to the absence of the rotational modes of deuterium.

TABLE 17

P cm.Hg	λ microns	V ideal (cm/sec)	V^2 X 10^{-8} $(cm/sec)^2$	log f/p
151	3024.2	28220	7.96_4	4.670
138	3028.6	28252	7.98_2	4.709
124	3032.4	28273	7.99_4	4.755
109	3035.8	28292	8.00_4	4.812
98	3041.2	28334	8.02_8	4.857
85	3046.0	28367	8.04_7	4.919
75	3048.2	28378	8.05_3	4.974
63	3055.6	28437	8.08_7	5.050
53	3065.0	28516	8.13_2	5.124
43	3068.6	28540	8.14_5	5.215

In this mixture it was assumed that there were two independent relaxation processes, namely the vibrational relaxation of CO_2 by self collisions and collisions with deuterium, and the rotational relaxation of deuterium:-

$$CO_2^{*} + CO_2 \longrightarrow CO_2 + CO_2 + 667\ cm^{-1} \quad (1)$$

$$CO_2^{*} + D_2 \longrightarrow CO_2 + D_2 + 667\ cm^{-1} \quad (2)$$

$$D_2^{\dagger} + D_2 \longrightarrow D_2 + D_2 + \text{rotational quanta} \quad (3)$$

$$D_2^{\dagger} + CO_2 \longrightarrow D_2 + CO_2 + \text{rotational quanta} \quad (4)$$

where * represents vibrational excitation

† represents rotational excitation

It is further assumed that CO_2 was an inefficient collision partner for deuterium. The variation of V^2 with W and τ for parallel excitation of different degrees of freedom is given (28) by:-

$$V^2 = RT/M \left(1 + \frac{R.A}{A^2 + B^2} \right)$$

where

$$A = C_\infty + \frac{C_{VIB\ CO_2}}{1 + W^2\tau_1^2} + \frac{C_{ROT\ D_2}}{1 + W^2\tau_2^2}$$

and

$$-iB = \frac{C_{VIB\ CO_2}\ x\ iW\tau_1}{1 + W^2\tau_1^2} + \frac{C_{ROT\ D_2}\ x\ iW\tau_2}{1 + W^2\tau_2^2}$$

where C_∞, $CvibCo_2$, $CrotD2$ are the specific heat contributions from translational mode + rotational modes of CO_2, vibrational modes in CO_2 and rotational modes in D_2 respectively, and where τ_1, τ_2 are the overallrelaxation times of CO_2 and D_2 respectively,

that is:-

$$\frac{1}{\tau_1} = \frac{0.925}{6.8} + \frac{0.075}{\tau CO_2D_2}$$

$$\frac{1}{\tau_2} = \frac{0.075}{0.015}$$

The figure of 0.015 μsec for τrot D_2 at 303° K was extrapolated from data at 273°K by Stewart and Stewart (26), assuming a temperature dependence in the normal sense, as indicated by Sluijter (29).

The results fit the above relation for the value:-

$\tau CO_2D_2 = 0.09 \pm 0.02$ μsecs. at 303°K and 1 atmosphere pressure.

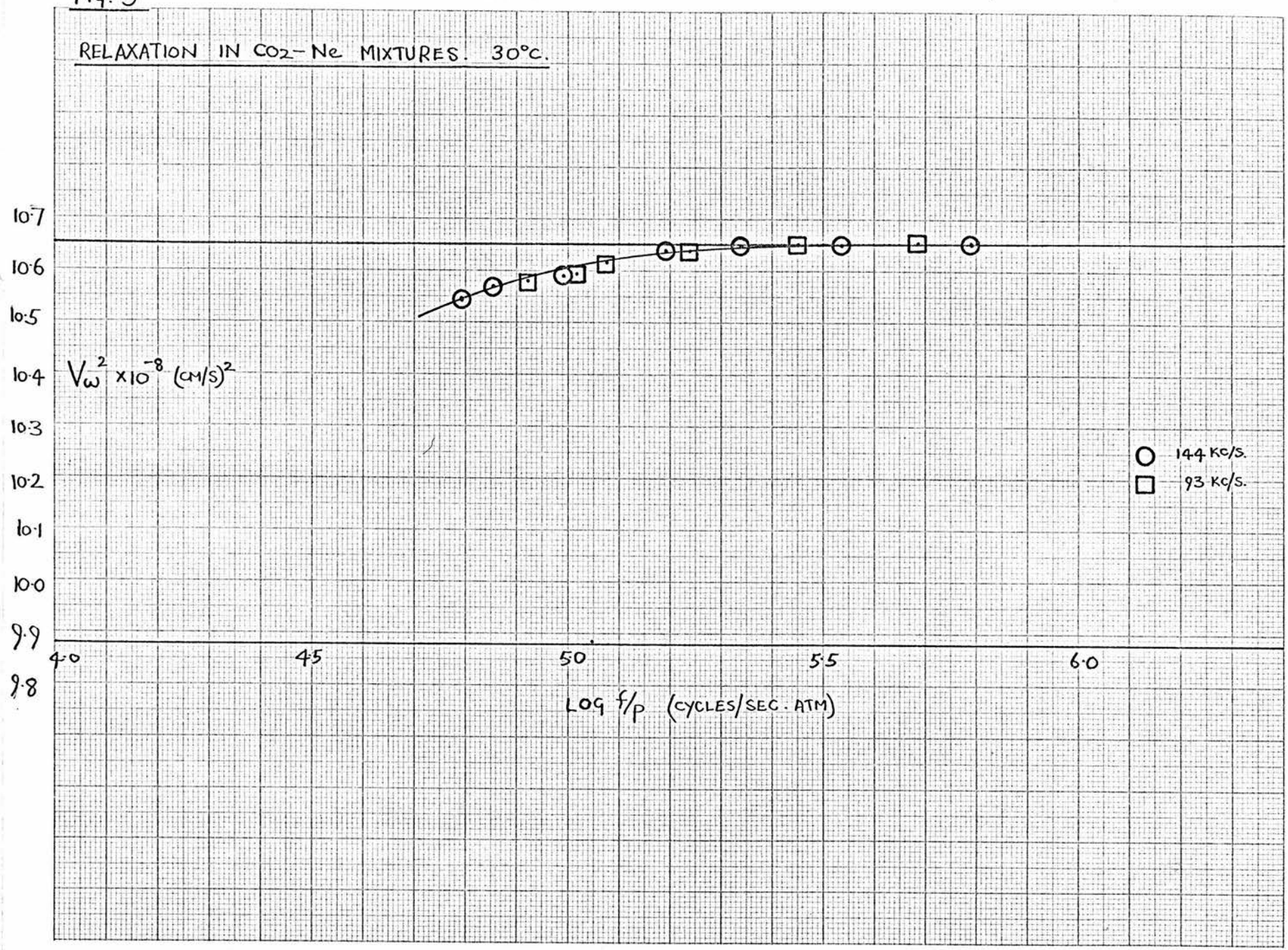
SECTION B

This section comprises those mixtures with relaxation times larger than that of CO_2, namely CO_2 with neon, argon and Xenon. In order to obtain f/p values of 50 - 60 kc/sec. atm. using crystals with frequencies around 100 kc/s, pressures up to 2.4 atmospheres were employed; they were achieved using the pressure pump described in the experimental section.

1. CARBON DIOXIDE - NEON

Preliminary measurements of a CO_2Ne mixture indicated that CO_2Ne collisions were less efficient than pure CO_2 collisions. Bearing in mind the problems involved in both accurately defining the overall relaxation time τ and ensuring that $XNe/\tau CO_2Ne$ was of the same order of magnitude as $(1 - XNe)/\tau CO_2$, two mixtures were used, of composition 6 - 4 and 1 - 1, and two crystals, of frequency 93 and 144 kc/s. The separate results are shown in Tables 18 and 19, and are plotted on a standardised 60 - 40 mixture graph in Fig 9 , assuming that the overall relaxation time for the process is linearly dependent on the mole fraction of inert gas.

FIG: 9


RELAXATION IN CO2 – Ne MIXTURES. 30°C.
10·7
10·6
10·5
10·4
10·3
10·2
10·1
10·0
9·9
9·8
$V_\omega^2 \times 10^{-8}$ (CM/S)^2
4·0
4·5
5·0
5·5
6·0
LOG f/p (CYCLES/SEC. ATM)
144 KC/S.
93 KC/S.

SET A

FREQUENCY = 93,170 c/s TWC = 14 μ

COMPOSITION: CO_2 = 50.6% $Vo^2 = 10.93_4 \times 10^8 (cm/sec)^2$

Ne = 49.4% $Voo^2 = 11.73_1 \times 10^8 (cm/sec)^2$

TABLE 18

P cm.Hg	λ microns	V ideal (cm/sec)	$V^2 \times 10^{-8}$ $(cm/sec)^2$	log f/p
84	3666.0	34152	11.66_4	4.93
71	3668.0	34171	11.67_7	5.002
60	3671.6	34205	11.69_9	5.075
41	3675.0	34236	11.72_1	5.241
25	3677.0	34255	11.73_4	5.452
15	3676.3	34248	11.72_9	5.688

SET B

FREQUENCY = 144,500 c/s TWC = 2.7 μ

COMPOSITION: CO_2 = 61.6% $Vo^2 = 9.87_5 \times 10^8 (cm/sec)^2$

Ne = 38.4% $Voo^2 = 10.65_5 \times 10^8 (cm/sec)^2$

TABLE 19.

P cm.Hg	λ microns	V ideal (cm/sec)	$V^2 \times 10^{-8}$ $(cm/sec)^2$	log f/p
178	2246.7	32479	10.54_9	4.790
151	2249.7	32520	10.57_6	4.862
112	2252.1	32552	10.59_6	4.992
71	2257.9	32633	10.64_9	5.193
51	2258.7	32642	10.65_5	5.331
31	2258.3	32634	10.65_6	5.550
20	2259.1	32646	10.65_8	5.740

The results fit an overall relaxation time:- $\tau = 8.1 \pm 0.4$ μsec.

so that $\tau CO_2Ne = 12 \pm 3$ μsec. at 303°K and 1 atmosphere pressure.

SECTION B.

2. CARBON DIOXIDE - ARGON.

Two mixtures were made up and measured using the 92.89 kc/s crystal, namely a 60 - 40 and 80 - 20 mole percent CO_2 - Argon respectively. The results are shown in Tables 20 and 21 and displayed in a standard graph in Fig (10).

SET A.

FREQUENCY = 92,890 c/s TWC = 10 μ.

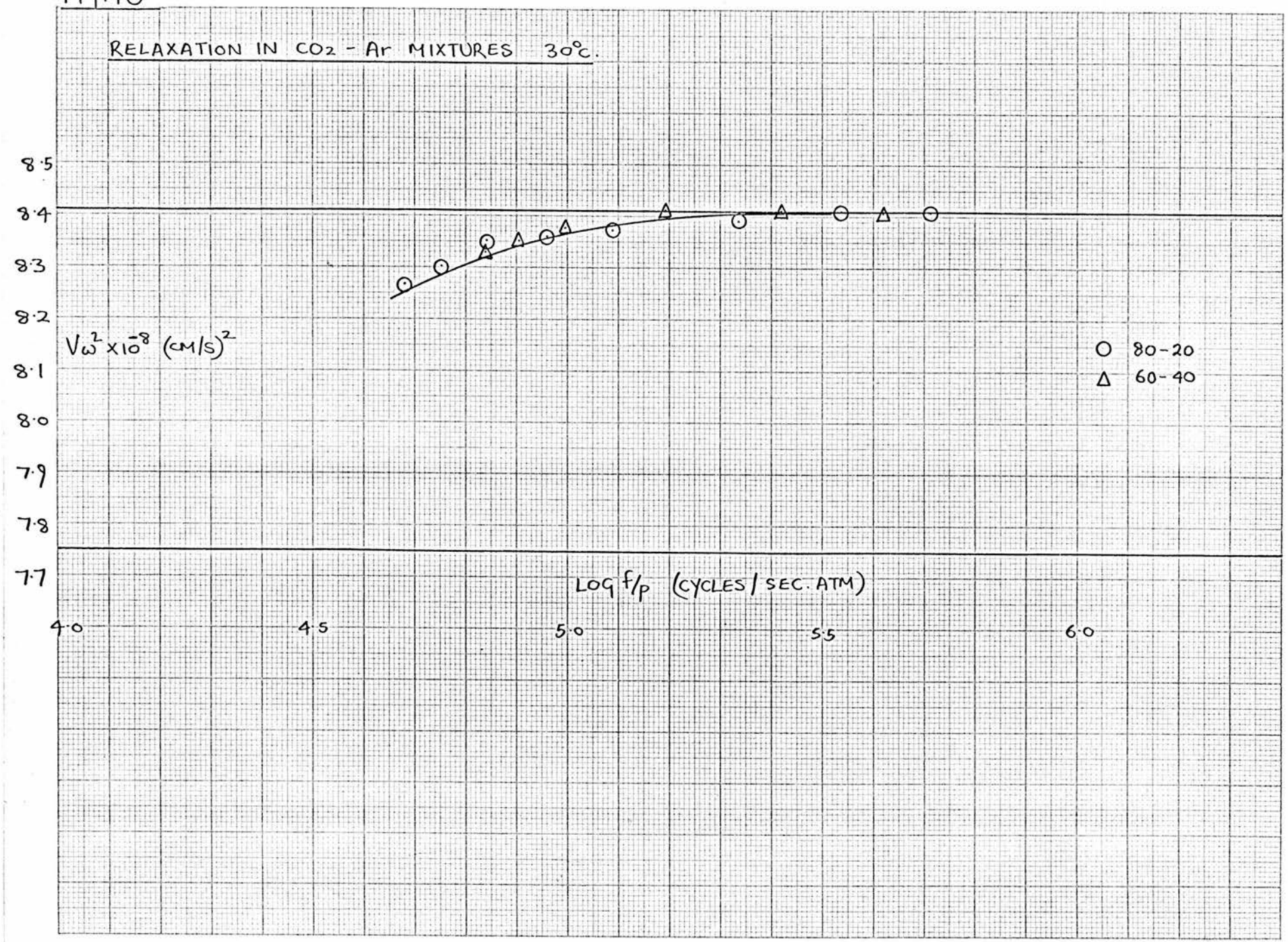
COMPOSITION: CO_2 = 59.7% $Vo^2 = 8.13_5 \times 10^8 (cm/sec)^2$

Ar = 40.3% $Voo^2 = 8.77_2 \times 10^8 (cm/sec)^2$

TABLE 20.

P cm.Hg	λ microns	V ideal (cm/sec)	V^2 X 10^{-8} $(cm/sec)^2$	log f/p
148	3174.4	29538	8.72_5	4.680
102	3180.5	29579	8.74_9	4.840
83	3183.1	29598	8.76_0	4.904
71	3186.7	29625	8.77_6	5.000
52	3187.9	29630	8.77_9	5.133
45	3186.5	29615	8.77_0	5.200
27	3187.3	29617	8.77_2	5.420
17	3186.9	29610	8.76_8	5.620

FIG: 10


RELAXATION IN CO2 - Ar MIXTURES 30°C.
8·5
8·4
8·3
8·2
8·1
8·0
7·9
7·8
7·7
$V\omega^2 \times 10^{-8}$ (CM/S)^2
O 80-20
Δ 60-40
4·0
4·5
5·0
5·5
6·0
LOG f/p (CYCLES / SEC. ATM)

SET B .

COMPOSITION: CO_2 = 79.4% $Vo^2 = 7.75_0 \times 10^8 (cm/sec)^2$

Ar = 20.6% $Voo^2 = 8.41_0 \times 10^8 (cm/sec)^2$

TWC = 9.4 μ

TABLE 21.

P cm.Hg	λ microns	V ideal (cm/sec)	V^2 X 10^{-8} $(cm/sec)^2$	log f/p
147	3087.2	28755	8.26_9	4.68
124	3095.2	28817	8.30_4	4.75
101	3105.8	28904	8.35_4	4.84
80	3108.6	28919	8.36_3	4.95
37	3112.8	28946	8.37_9	5.09
32	3117.4	28975	8.39_6	5.34
21	3121.4	29007	8.41_4	5.53
14	3121.0	28999	8.40_9	5.70

The minimum relaxation time which can be fitted to the result is:-

$$\tau = 8.2 \ \mu secs.$$

so that the relaxation time for CO_2- Ar interaction must be reported as

$\tau\, CO_2Ar > 30\mu sec.$ at 303°K and 1 atmosphere pressure.

SECTION B.

3. CARBON DIOXIDE - XENON.

One 50 - 50 mixture was measured at 83.78 kc/s. The results are shown in Table 22.

FREQUENCY = 83,780 c/s VOLTAGE=10 SENSITIVITY = 1. TWC = 3.2μ.
COMPOSITION: $C\textcircled{O}_2$= 49.1% $V_o^2 = 4.05_8 \times 10^8 (cm/sec)^2$
Xe = 50.9% $V_\infty^2 = 4.34_8 \times 10^8 (cm/sec)^2$

TABLE 22

P cm.Hg	λ microns	V ideal (cm/sec)	$V^2 \times 10^{-8}$ $(cm/sec)^2$	log f/p
92	2479.4	20830	4.33_9	4.84
78	2483.0	20850	4.34_6	4.91
64	2481.8	20829	4.33_8	4.99
54	2483.2	20835	4.34_1	5.07
43	2486.4	20859	4.34_9	5.17
35	2490.1	20882	4.36_1	5.26
30	2485.9	20843	4.34_4	5.33
25	2487.9	20860	4.35_1	5.41
21	2488.0	20852	4.34_8	5.49
17	2489.4	20863	4.35_3	5.57
14	2488.1	20851	4.34_8	5.65

Here again only a minimum relaxation time can be fitted to the results, that is τ = 11.4 μsecs. giving a relaxation time for $C\textcircled{O}_2Xe$ of $\tau \gg 30\mu$secs. at 303°K, 1 atmosphere pressure.

THE COLLECTED RESULTS, 303°K.

The results have been expressed as relaxation times and the number of collisions required for de-excitation Z_{10}. The symbol β corresponds to the relaxation time of the lowest mode, (specific heat C_1) and is related to the measured relaxation time by the equation:

$$\beta = \tau \quad C_1 vib \,/ \sum_s C_s \, vib$$

The collision number Z_{10} is given by

$$Z_{10} = Z_{AB} \beta \left(1 - \exp \left(-h\nu/kT \right) \right)$$

where $$Z_{AB} = 2n \left(\frac{\sigma_A + \sigma_B}{2} \right)^2 \left(\frac{2\pi kT (MA + MB)}{MA\ MB} \right)^{\frac{1}{2}}$$

TABLE 23.

GAS	τ μsec.	β μsec.	$Z_{AB} \times 10^{-9}$ collisions/molecule per second.	Z_{10} collisions/molecule $\times 10^{-3}$
CO_2D_2	0.08	0.074	13.8	1 ± 1
CO_2He	0.38	0.35	12.9	4.3 ± 0.5
CO_2Ne	12	11.1	6.8	72 ± 20
CO_2Ar	>30	>28	6.7	>179
CO_2CO_2	6.8	6.3	8.3	52 ± 3
CO_2Xe	$\gg 30$	$\gg 28$	6.3	$\gg 169$

METHANE AND MIXTURES, 303°K.

Significantly more accurate values of λ were obtained in methane and mixtures due to the smaller absorption coefficient, which itself depends on the relaxing specific heat. No error limits are included in the Tables, but errors arise in the following way, taking results for CH_4 as an example.

% error in λ mean	= 0.025
% error in λ with TWC	= 0.038 = error in $V_{obs.}$
% error accumulated in idealisation	= negligible.
% error in V^2	$\doteq$ 0.076
	= $\pm$ 0.015 x 10^8 (cm/s)^2

Errors in τ values were determined by inspection of the fit of individual points to a set of theoretical dispersion curves.

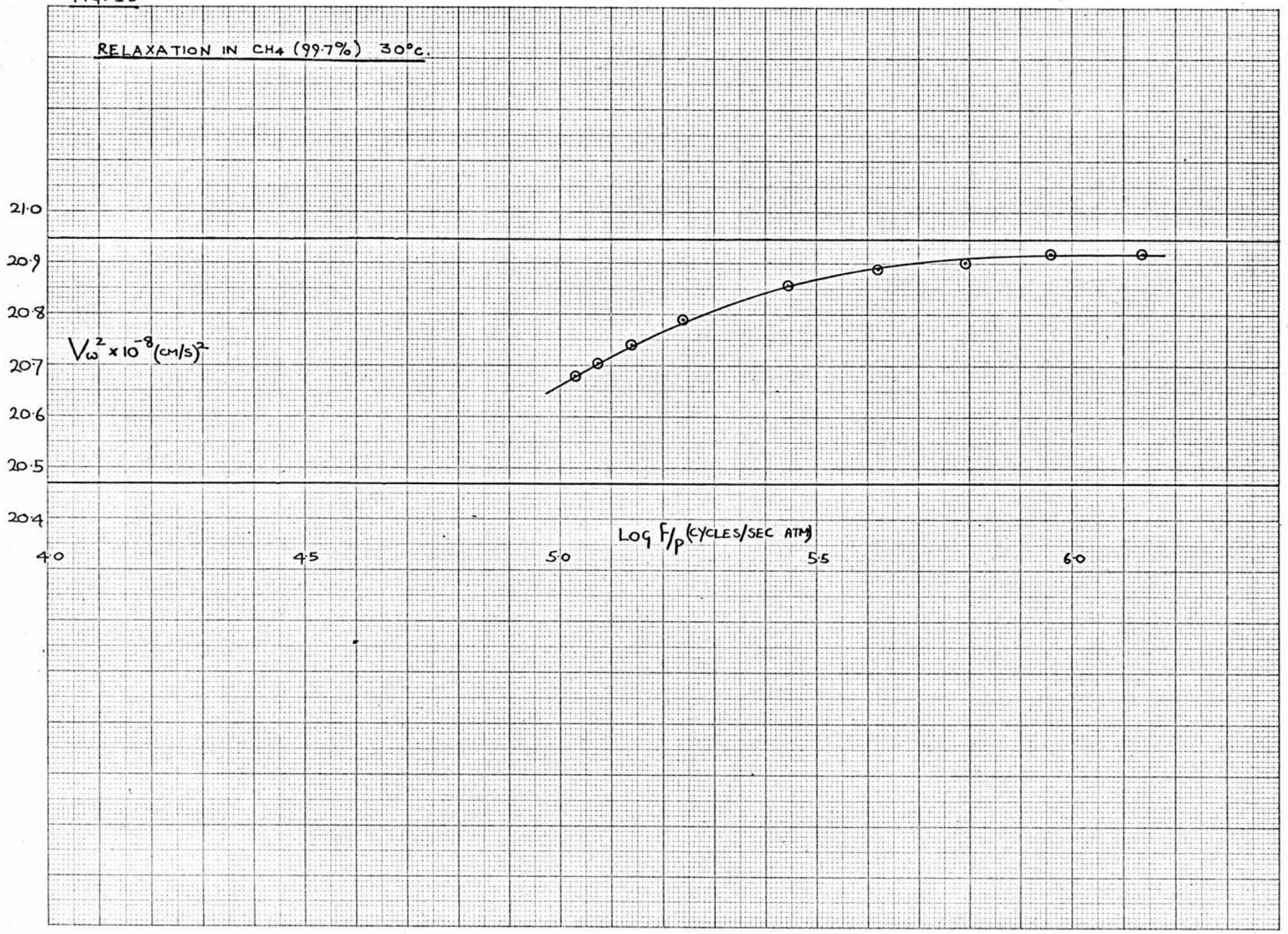
1. METHANE.

A 144 kc/s crystal was used over an f/p range of 106 - 1370 kc/s. atm, and the results are shown in Table (24) and Fig (11).

The sample contained 0.3% hydrocarbon impurities, which explains the discrepancy between the observed $V_\infty^2 = 20.92_0 \times 10^8$ (cm/sec)^2 and the calculated value of $V_\infty^2 = 20.94_8 \times 10^8$ (cm/sec)2.

Dispersion curves were drawn up assuming single dispersion using $V_\infty^2 = 20.92_0 \times 10^8$(cm/sec)^2 and $V_o^2 = 20.43_6 \times 10^8$(cm/sec)^2, that is, assuming that the relaxing specific heat was identical with that of the pure methane.

FIG: 11


RELAXATION IN CH4 (99·7%) 30°C.
21·0
20·9
20·8
20·7
20·6
20·5
20·4
$V_\omega^2 \times 10^{-8}$ (cm/s)^2
4·0
4·5
5·0
5·5
6·0
Log F/p (CYCLES/SEC ATM)

FREQUENCY = 144,500 c/s VOLTAGE = 6 SENSITIVITY = 0.5
SCAN SPEED = 1200 μ /min. CHART SPEED = 8"/min. TWC = 7.6 μ .

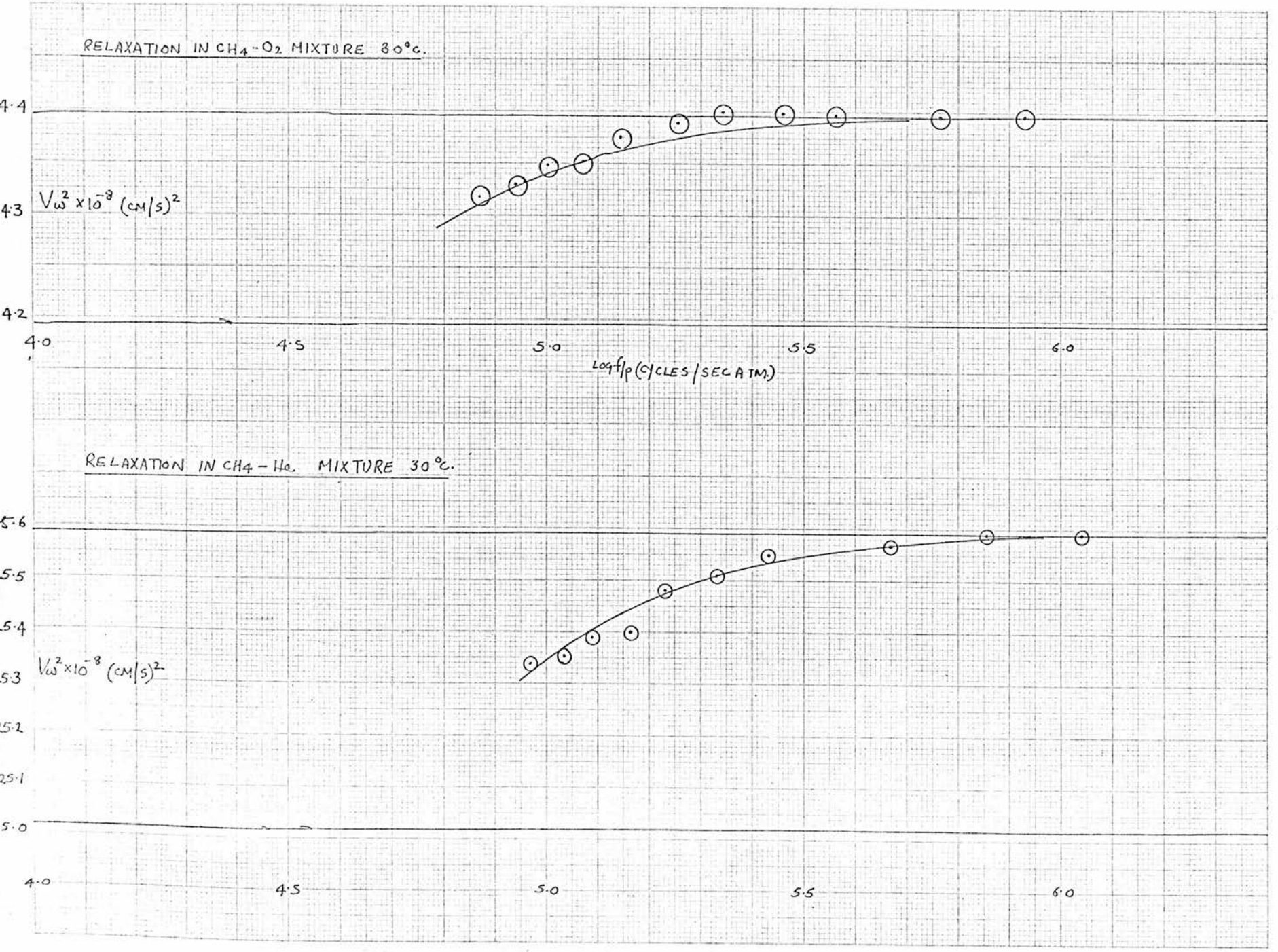
TABLE 24.

P cm.Hg	λ microns	V ideal (cm/sec)	$V^2 \times 10^{-8}$ $(cm/sec)^2$	log f/p
103	3144.8	45480	20.68_4	5.027
93	3146.4	45499	20.70_2	5.072
79	3149.8	45544	20.74_3	5.143
63	3153.6	45592	20.78_6	5.241
39	3159.8	45673	20.86_0	5.449
26	3162.2	45704	20.88_9	5.625
18	3163.0	45712	20.89_6	5.790
12	3165.0	45738	20.92_0	5.961
8	3165.0	45747	20.91_9	6.137

The relaxation time defined in this way is

$\tau = 1.7 \pm 0.1$ μsecs. at 303°K and 1 atmosphere pressure.

FIG: 12


RELAXATION IN $CH_4 - O_2$ MIXTURE 30°C.
4·4
4·3
$V\omega^2 \times 10^{-8}$ (CM/S)^2
4·2
4·0
4·5
5·0
5·5
6·0
Log f/p (CYCLES/SEC ATM.)
RELAXATION IN $CH_4 - He$. MIXTURE 30°C.
5·6
5·5
5·4
5·3
$V\omega^2 \times 10^{-8}$ (CM/S)^2
5·2
5·1
5·0
4·0
4·5
5·0
5·5
6·0

2. METHANE - OXYGEN.

A mixture of composition 1/1 was made up on the assumption that oxygen would be a very inefficient collision partner for methane. Measurements were made at 144 kc/s and are shown in Table 25 and Fig 12.

FREQUENCY = 144,500 c/s TWC = 4μ

COMPOSITION CH_4 51.0% $Vo^2 = 14.19_5 \times 10^8 (cm/sec)^2$

O_2 49.0% $Voo^2 = 14.39_7 \times 10^8 (cm/sec)^2$

TABLE 25.

P cm.Hg	λ microns	V ideal (cm/sec)	$V^2 \times 10^{-8}$ $(cm/sec)^2$	log f/p
149	2617.8	37843	14.32_1	4.868
126	2619.0	37858	14.33_2	4.939
109	2620.6	37879	14.34_8	5.003
93	2621.2	37886	14.35_3	5.072
78	2623.4	37916	14.37_6	5.147
61	2624.8	37934	14.38_9	5.255
50	2625.8	37948	14.40_0	5.342
38	2625.4	37940	14.39_4	5.464
31	2625.6	37943	14.39_7	5.556
19	2625.8	37944	14.39_7	5.769
13	2625.8	37944	14.39_7	5.927

The results fit an overall relaxation time $\tau = 2.8 \pm .3$ μsec., giving $\tau_{CH_4O_2} = 7.8 \pm 4$μsec. at 303°K and 1 atmosphere pressure.

3. METHANE - HELIUM.

The choice of helium as a collision partner for methane illustrates the considerations involved in mixture work. It was decided to study the efficiency of inert gas with methane in order to investigate the proposal made by Cottrell and Matheson (3) concerning rotational transfer in methane. Because of the small dispersion region in methane, mixtures with gases whose specific heats are less than that of methane require careful planning. The size of the dispersion region $\triangle(V)^2$ depends on 1/M mix and $(1/C_\infty - 1/C_o)$ mix; thus neon would be unsuitable on two counts. First, its mass is larger than that of methane, so reducing $\triangle(V)^2$, and secondly, its efficiency was thought to be less than that of methane. Their combined effect would be to produce a very flat dispersion curve with a consequently inaccurate relaxation time. Helium on the other hand can be used to high concentrations without reducing very much the size of the dispersion region. After preliminary measurements had shown that helium was not an efficient collision partner with methane, a final composition of 79% CH_4/21% He was made up in the usual way, and high pressure pumping was used to cover approximately half the dispersion region. The results are shown in Table (26) and displayed in Fig (12).

FREQUENCY = 144,500 c/s TWC = 9.5 μ.

COMPOSITION: CH_4 = 78.8% $Vo^2 = 25.02_7 \times 10^8$ (cm/sec)^2

He = 21.2% $Voo^2 = 25.59_4 \times 10^8$ (cm/sec)^2

TABLE 26.

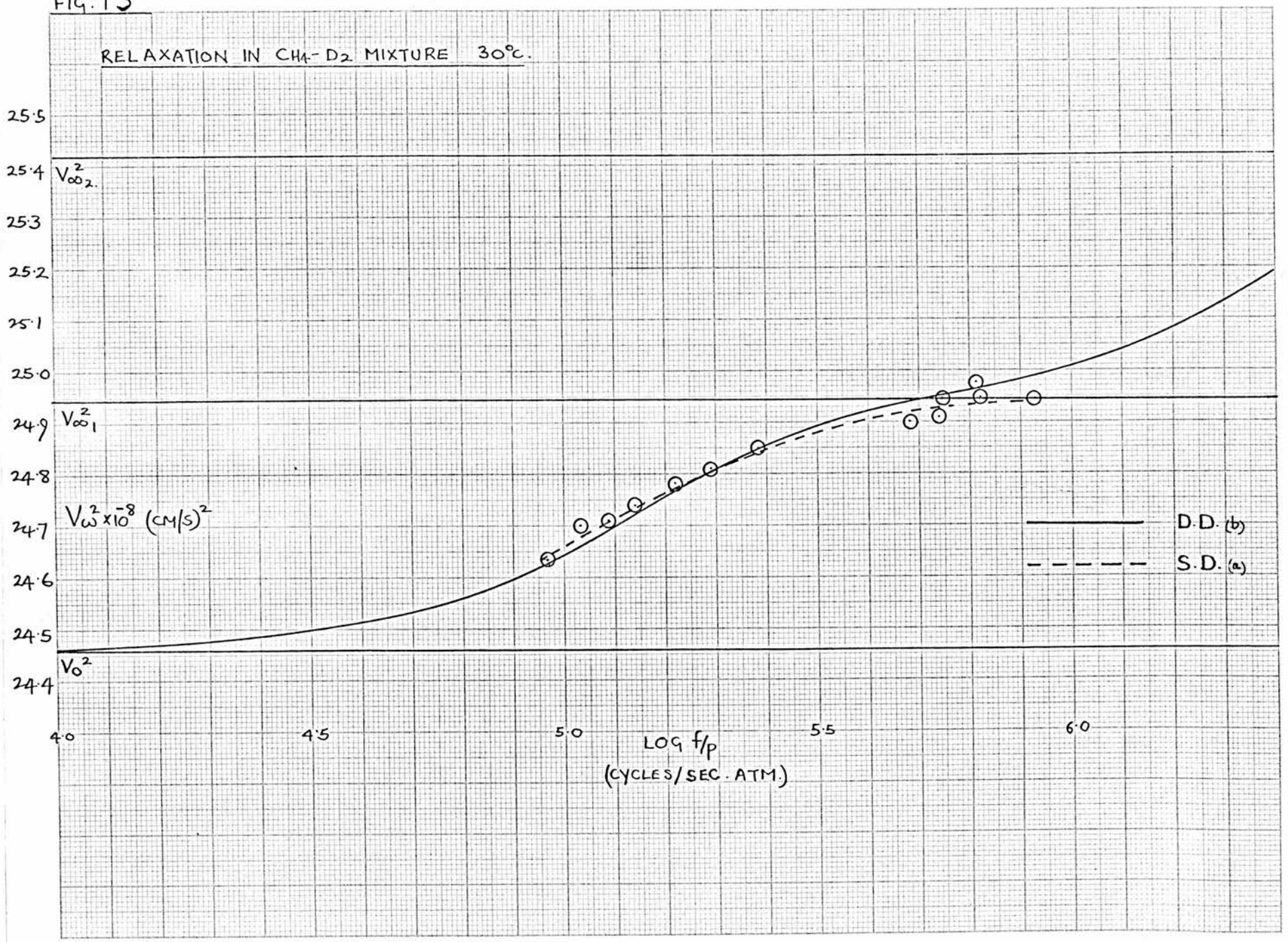
P cm.Hg	λ microns	V ideal (cm/sec)	$V^2 \times 10^{-8}$ (cm/sec)^2	log f/p
117	3483.1	50334	25.33_5	4.97
102	3484.9	50359	25.36_0	5.03
89	3486.7	50385	25.38_6	5.09
76	3488.1	50405	25.40_7	5.16
65	3493.3	50480	25.48_2	5.23
50	3496.1	50521	25.52_4	5.34
41	3498.1	50548	25.55_2	5.43
24	3498.9	50559	25.56_2	5.65
15	3501.3	50594	25.59_6	5.85
10	3500.9	50588	25.59_1	6.04

The results fit an overall relaxation time

$$\tau = 1.9 \pm 0.1 \ \mu\text{sec.}$$

so that $\tau CH_4He = 3.4 \pm 2$ μsec. at 303°K and 1 atmosphere pressure.

FIG: 13


RELAXATION IN CH4 - D2 MIXTURE 30°C.
25·5
25·4
$V^2_{\infty 2}$
25·3
25·2
25·1
25·0
24·9
$V^2_{\infty 1}$
24·8
$V^2_\omega \times 10^{-8}$ (CM/S)^2
24·7
24·6
24·5
V_0^2
24·4
4·0
4·5
5·0
5·5
6·0
LOG f/p
(CYCLES/SEC. ATM.)
D.D. (b)
S.D. (a)

4. METHANE - DEUTERIUM.

An 80/20 mixture was measured at 144.5 kc/s using high pressure pumping. The results are shown in Table (27) and Fig (13).

FREQUENCY = 144,500 c/s TWC = 9 μ.

COMPOSITION: CH_4 = 79.6% $Vo^2 = 24.45_9 \times 10^8 (cm/sec)^2$

D2 = 20.4% $V_{1\infty}^2 = 24.94_5 \times 10^8 (cm/sec)^2$

$V_{2\infty}^2 = 25.42_1 \times 10^8 (cm/sec)^2$

where the suffixes have the same meaning as in the Co_2-D_2 92/8 section.

TABLE 27.

P cmHg.	λ microns	V ideal (cm/sec)	$V^2 \times 10^{-8}$ $(cm/sec)^2$	log f/p
118	3434.2	49633	24.63_4	4.970
101	3439.4	49707	24.70_8	5.037
88	3440.0	49715	24.71_6	5.097
78	3441.6	49737	24.73_8	5.149
67	3445.0	49786	24.78_6	5.215
57	3446.8	49811	24.81_1	5.286
46	3449.4	49848	24.84_8	5.378
23	3453.0	49898	24.89_8	5.679
20	3455.8	49938	24.93_8	5.740
17	3456.6	49949	24.94_9	5.823
13	3456.6	49949	24.94_9	5.927

The results were analysed assuming two extreme conditions for the overall scheme:-

$CH_4^* + CH_4 \longrightarrow CH_4 + CH_4 + 1306\ cm^{-1}$ (1)

$CH_4^* + D_2 \longrightarrow CH_4 + D_2 + 1306\ cm^{-1}$ (2)

$D_2^\dagger + D_2 \longrightarrow D_2 + D_2 +$ rotational quanta (3)

$D_2^\dagger + CH_4 \longrightarrow D_2 + CH_4 +$ rotational quanta (4)

a) . Reaction (4) is at least as efficient as deuterium in rotational relaxation in deuterium. This condition could be achieved if the rotational modes of methane played an important role, that is, if rotation-rotation transfer to methane were rapid. Over the experimental f/p range this would correspond to the single dispersion of reactions (1) and (2) involving only the vibrational specific heat of methane.

Analysed in this way τ overall = 1.5 μsecs.

so that $\tau\ CH_4 - D_2$ = 1 $\pm$ 0.5 μsecs. at 303°K, and 1 atmosphere pressure

b). Reaction (4) is completely inefficient. In this case an analysis similar to that used for the CO_2D_2 results was carried out using the following values.

$$\frac{1}{\tau_1} = \frac{0.796}{1.7} + \frac{0.204}{\tau CH_4D_2}$$

$$\frac{1}{\tau_2} = \frac{0.204}{0.015}$$

The results fit curves drawn for

$\tau\ CH_4 - D_2$ = 1 μsec.

Thus, no matter what assumption is made concerning reaction (4), τ CH_4 - D_2 is unaffected. The f/p range used did not extend sufficiently to allow a decision to be made concerning reaction (4), although it is unlikely that assumption (b) represents the true situation.

COLLECTED RESULTS, 303°K.

Assuming that equilibration occurs through the 1306 cm^{-1} mode, the following results have been calculated from the experimental data (Table 28).

TABLE 28.

GAS	τ μsec.	β μsec.	$Z_{AB} \times 10^{-9}$ collision/molecule per second	Z_{10} collision/molecule $\times 10^{-3}$
CH_4CH_4	1.7	1.3	10.1	13 ± 1
CH_4-O_2	7.8	5.8	8.2	46±26
CH_4-He	3.4	2.5	11.3	28 ± 20
CH_4-D_2	1.0	0.75	12.2	9 ± 6

CHAPTER 6.

DISCUSSION : PART A.

THEORETICAL CONSIDERATIONS.

By comparing experimental results with those calculated from well established theory it is possible to gain information about the mechanisms of energy transfer in the molecules under consideration. If significant discrepancies exist between experimental and theoretical results they may be interpreted in two ways. First, if the discrepancy can be removed by introducing refinements within the original theoretical framework, then the mechanism of energy transfer is most probably that envisaged in the theory. Secondly, if the discrepancy cannot be removed in this way, new schemes of energy transfer can be put forward.

The purpose of this section is, therefore, to define the mechanism of energy transfer proposed by the theory, and to take note of approximations made in the theory and consequently the conditions under which it is not valid. In this way a valid method of comparing experimental and theoretical results can be derived.

Two explicit expressions exist for the transition probability of vibrational excitation and de-excitation during a collision. They are the Cottrell-Ream expression (7) which is a semi-classical approach, and the Schwartz, Slawsky and Herzfeld SSH expression (30), which is a quantum mechanical solution of the problem. The expressions are practically the same, and the ratio of the results they give for transition probabilities per collision over a range of initial relative energies is approximately unity(28). In the present work the Cottrell-Ream expression has been used. The model consists of a diatomic molecule, assumed to be a harmonic oscillator, in collision with a structureless particle,

an atom, and the transition probability for vibrational excitation during an encounter is determined by calculating the probability that the oscillator will be in an excited state after it has been perturbed by a time-dependent force. Time-dependent perturbation theory is used. The probability that the oscillator will be in a state k after perturbation by a potential $x\,F(t)$ is given:-

$$C_k^2 = \frac{1}{\hbar^2} \left| X_{mk} \right|^2 \left| \int_{-\infty}^{\infty} F(t) \exp(2\pi i \nu t)\, dt \right|^2$$

x_{mk} is the matrix element corresponding to the x-dependence of the perturbation, and for de-excitation of the vibrational state $1 \longrightarrow 0$ is

$$x_{10}^2 = \frac{\hbar}{(4\pi M \nu)}$$

where M is the reduced mass of the oscillator, and ν is the vibration frequency.

Two limitations of the theory immediately arise; First, the theory is only valid for small perturbations, that is, for small transition probabilities. Secondly, approximations are introduced when the theory is applied to polyatomic molecules because the meaning of the factor M is less clear. In the simplest case, that of a homonuclear diatomic molecule of mass 2m in collision with a particle mass 2m, the reduced mass of the collision μ is equal to m, and M is equal to m/2. In the following calculations this value is assumed, and this eliminates the possibility of absolute comparisons of experimental and theoretical results. The final expression for the transition probability is:-

$$f10 = \frac{4\pi}{\sqrt{3}} \; NB \; r_o^2 \; V^* \; \exp\left(-3y^* + \frac{h\nu}{2kT} + \frac{\varepsilon}{kT} \right)$$

where $$B = \frac{32\pi^4 \mu^2 \nu}{h \alpha^2 M}$$

$$V^* = \left(\frac{4\pi^2 kT \nu}{\alpha \mu} \right)^{1/3}$$

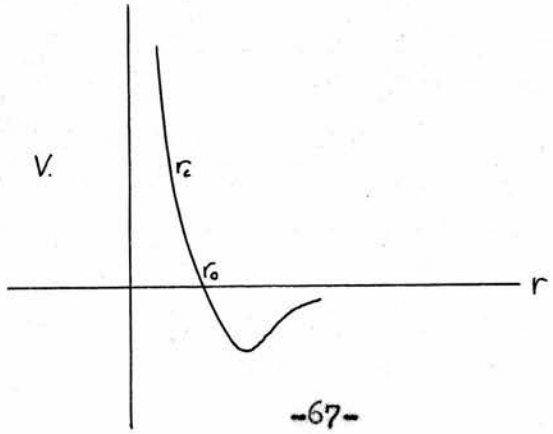
$$y^* = \left(\frac{2\pi^4 \mu \nu^2}{\alpha^2 kT} \right)^{1/3}$$

It represents the solution obtained using an exponential repulsive potential

$$V = Ae^{-\alpha r_o} - \varepsilon$$

for which the perturbation integral can be integrated analytically. Herzfeld and co-workers (30) have shown that a numerical value for α can be found by fitting the potential to a Lennard-Jones 6 - 12 potential. In this work, the curve is fitted at two points, as in Fig (14), according to the method of de Wette and Slawsky (31).

FIG14



The factor α is then obtained from the simultaneous equations

$$0 = Ae^{-\alpha r_o} - \varepsilon$$

$$E_m = Ae^{-\alpha r_c} - \varepsilon$$

where E_m is the most effective energy of approach and r_c the stopping point for a particle of energy E_m.
The important part of the potential for energy transfer is between r_o and r_c, the repulsive part governed by the twelfth power of the Lennard-Jones expression. This index was chosen for mathematical convenience and therefore introduces another uncertainty factor into the expression for the transition probability. In view of the approximations mentioned above, the method chosen to compare experimental and theoretical results was to compare

$$\left(\frac{P_{10}\ CO_2X}{P_{10}\ CO_2} \right) \text{ Theory with } \left(\frac{P_{10}\ CO_2X}{P_{10}\ CO_2} \right) \text{ Expt.}$$

Transitions probabilities have been worked out for each pure gas and mixture in both the CO_2 and CH_4 series using Lennard-Jones data from reference (11), which in turn came from room temperature virial data.
The results of the first step, the derivation of α Lennard-Jones values, are shown in Table (29).

TABLE (29)

GAS	ε/k deg.	σ A^o	α L - J A^o - 1
CO_2 - D_2	77	3.68	5.33
CO_2 - He	34	3.56	5.36
CO_2 - Ne	82	3.62	5.35
CO_2 - Ar	151	3.95	5.02
CO_2 - CO_2	189	4.49	4.43
CO_2 - Xe	204	4.29	4.67
CH_4 - CH_4	148	3.82	5.12
CH_4 - O_2	132	3.70	5.25
CH_4 - He	30	3.22	5.86
CH_4 - D_2	68	3.34	5.78

The results of the final step, the calculation of β , are shown in Table 30.

TABLE 30.

GAS	μ a.m.u.	B	V^* x 10^5 cm/sec.	Y^*	β μSec.	Z_{10} collisions
CO_2-D_2	3.67	67.8	2.19	3.43	0.0013	18
CO_2-He	3.67	67.4	2.19	3.42	0.00155	20
CO_2-Ne	13.8	952	1.42	5.33	0.044	300
CO_2-Ar	20.9	2480	1.23	6.39	0.31	2,080
CO_2-CO_2	22	3530	1.21	7.06	1.11	9,200
CO_2-Xe	32.9	7100	1.06	7.80	6.0	37,800
CH_4CH_4	8	1873	2.12	7.14	0.535	5,400
CH_4-O_2	10.7	3200	1.97	7.75	2.31	18,950
CH_4-He	3.2	229	2.89	4.80	0.006	67
CH_4-D_2	3.2	236	2.89	4.85	0.0056	67

DISCUSSION : PART B.

THE CARBON DIOXIDE SERIES.

RELAXATION IN CARBON DIOXIDE.

The value of 6.8 μsec. for vibrational relaxation in pure CO_2 at30°c agrees well with measurements from a large number of sources, including the most recent work (32), (33). When the results from the literature are plotted as log Z 10 against $T^{-1/3}$, there is a broad heavily populated band which defines the acceptable range of τ at 303°K as 5.0 - 7.2 μsecs. In gases which have a chemical affinity with water, such as CO_2, long values of the relaxation time are always to be preferred because water vapour has a strongly catalytic effect on their relaxation. Contamination with water can arise from two sources; first, it can be inadequately removed by the use of drying agents such as $CaCl_2$ or $CaSO_4$, and secondly, it is desorbed from the walls of the interferometer and can produce a significant decrease in V_{∞} within eight hours. In the second case the effect can be reduced by baking under high vacuum if the materials of the apparatus can withstand elevated temperatures.

Relaxation in CO_2 has been interpreted as a vibration-translation process in which energy from the upper modes quickly equilibrates with the 667 cm^{-1} mode, from which it is then transferred more slowly into translational modes. Two groups of workers (21), (34) claim to have detected double dispersion, corresponding to parallel excitation of the 667 cm^{-1} and 1351 cm^{-1} modes. Although the empirically established rule that double dispersion should be observed when $\nu_2 > 2\nu_1$ holds here, the almost exact resonance between the first harmonic of the 667 cm^{-1} and the 1351 cm^{-1} mode suggests that a series mechanism

would be very efficient. The range of f/p values used in the present work does not permit experimental comment on this problem, or on the question of rotational relaxation, which Holmes (35) finds to be very rapid.

In a recent paper Moore (2) has extended the vibration-rotation mechanism proposed by Cottrell and Matheson (3) to a large group of molecules with low moments of inertia, which lie around the lower line of the Lambert-Salter (36) plot. Carbon dioxide lies well on the upper line of molecules with large moments of inertia for which a vibration-translation scheme is most likely. However, certain additives have marked catalytic effects on CO_2 which cannot be explained by the simple vibration-translation process. The efficiency of CH_4 in de-exciting CO_2 has been explained by Moore in terms of a vibration-rotation process, which may also explain the high efficiency of H_2S (37) and Hcl (18).

RELAXATION IN CO_2 - INERT MIXTURES.

Of the inert gases argon and helium have been studied before in the literature (38) (39) (40). In all cases the value of $\tau\ CO_2He$ is lower than that obtained in the present work, although the most recent work, that of Bauer and Liska (40) gives a value of 0.33 μsec at 23° C with a reference value for CO_2 at 23°C of 6.5 μ sec. Again long relaxation times are to be preferred because in nearly all cases in the literature small proportions of helium have been used, so that any impurities present will represent only a very small percentage of the total composition. This means that inefficient impurities would have a negligible effect on the result, but efficient impurities, such as H_2O, would cause a significant reduction in the result.

The available data on CO_2- Ar are contradictory; Kneser and Roesler (39) found argon ten times less efficient than CO_2, whilst Wallmann (41) found it as efficient. On basic theoretical grounds Wallmann's result is more reasonable because argon is lighter than CO_2; nevertheless there is a body of experimental work which directly or indirectly supports the longer result.

(1) In the series of inert gases studied in the present work the experimental ratios are always less than those predicted by theory.

(2) Legvold and Amme (42) found argon inefficient in de-exciting the heavier $CH\ Cl\ F_2$ molecule.

(3) Argon is an inefficient collision partner for N_2O (43) which is a comparable molecule to CO_2.

Following the considerations on Page 68, experimental and theoretical ratios of transition probabilities per collision are shown in Table (31).

TABLE 31

X	V T THEORETICAL RATIO	EXPERIMENTAL RATIO	LJ α A^{-1}	* α A^{-1}
He	460	12	5.36	3.39
Ne	30	0.72	5.35	3.9
Ar	4.4	< 0.29	5.02	4.1
Xe	0.23	$\ll 0.31$	4.67	4.67

There are two possible ways in which the experimental-theoretical discrepancy can be explained.

The nature of the observations suggests that relaxation by self collision in CO_2 may follow a different and more efficient path to that of CO_2 in collision with inert gas atoms. Although there is no direct experimental evidence against this idea, neither a V V or V R scheme seem theoretically plausible in CO_2; moreover, a V T scheme is generally accepted for CO_2. Now since collision between CO_2 and inert gas atoms can only be explained in terms of a similar scheme, the source of the discrepancy between experiment and theory must be sought elsewhere, within the framework of V T theory.

According to the exponential term in the simple Landau-Teller expression, the efficiency of energy transfer depends on the sharpness of the encounter between the vibrator and its collision partner, that is, on their relative velocity, and on the rate of change of interaction potential with time during the encounter. Of these, the latter, represented by α, is the more arbitrary, as explained on page 68. and it is

reasonable to seek the source of the discrepancy in this factor. When the α values are adjusted to obtain agreement between the experimental and theoretical ratios $P_{10}(CO_2x/CO_2)$, the values α^* (Table 31) are obtained, indicating that the interactions between CO_2 and inert gases are softer than predicted by the Lennard-Jones expression. There is now evidence from molecular beam work that the repulsive 12th power may not represent the repulsive interaction between a molecule and an inert gas. Thus although a 12th power is suitable for H_2 - H_2 interactions, a 10th or 11th power appears to be more appropriate for H_2 - He and possibly H_2 - Ne collisions (44).

A similar approach has been used by McCoubrey, Milward and Ubbelohde (45). They plotted log Z_{10} from the literature for a large number of molecules against $T^{-1/3}$ and obtained α's from the slopes which were much larger than those derived from Lennard-Jones viscosity data. By incorporating refinements into the exponential of the Cottrell-Ream expression to account for symmetrization and attractive forces, α values of the order of 1.5 α Lennard-Jones were obtained, indicating that interactions between many molecules in homomolecular collisions are steeper than the Lennard-Jones predictions. Although neither this approach nor the present one involve the inclusion of the arbitrary reduced mass of the oscillator, neither approach is completely satisfactory; thus McCoubrey et al. assume that vibration-translation transfer adequately represents the de-activation process for each example, including CH_4 for which there is strong evidence of V R transfer. The present approach can be criticised because it relies on data at a single temperature.

RELAXATION IN CO_2D_2.

If the Landau-Teller theory is applicable to relaxation in CO_2-He not only in that it assumes a V T process, but also in that it can adequately represent the dynamics of the encounter between CO_2 and a particle of mass 4 a.m.u., it should predict a negligible difference between helium and deuterium. A comparison between the experimental and theoretical ratios of P_{10} (CO_2He /CO_2) and $P_{10}(CO_2D_2/CO_2)$, Table (32), shows that deuterium is approximately four times more efficient than helium. This is a significant result because the method of comparison eliminates the concept of the reduced mass of the oscillator, and it points to the operation of a different de-activation scheme in CO_2-D_2.

TABLE 32 .

X	$P_{10}(CO_2X/CO_2)$ THEORY	$P_{10}(CO_2X/CO_2)$ EXPERIMENTAL
D_2	510	52
He	460	12

A linear dependence of $\tau\ CO_2D_2$ on the mole fraction of D_2 was observed over the range 2 - 8% deuterium.
More extensive information can be obtained from the literature: Küchler (38) has studied the mole fraction and temperature dependence of $\tau\ CO_2H_2$ over the range 291-677°K, and has made a similar study of $\tau\ CO_2He$ over the range 291-685°K. More recently Winter (46) has studied the mole fraction dependencies of $\tau\ CO_2H_2$ and $\tau\ CO_2D_2$ over the

range 0.5 - 2% impurity, and the temperature dependences over the range 320-438°K. Both workers found a linear mole fraction dependence of the relaxation time. Küchler found hydrogen approximately eight times more efficient than helium, whereas conventional theory predicts a factor of two, and Winter's hydrogen result is shorter than his deuterium result by an amount greater than the theoretical prediction. A further interesting fact emerges that, whereas the temperature dependence of $Z_{10}CO_2He$ is slightly negative, in line with conventional theory, the temperature dependences of $Z_{10}CO_2H_2$ and CO_2D_2 are slightly positive in both Küchler's and Winter's work. For example Table (33).

TABLE 33 .

T°K	$Z_{10}CO_2He$	T°K	$Z_{10}CO_2H_2$	Reference.
291	3230	293	343	Küchler (38)
574	2850	342	337	
		416	368	
		586	431	
		677	366	

Three approaches to the results are possible:-

(1) Assuming very reasonable error limits, the temperature dependence of $Z_{10}CO_2H_2$ can be judged to be completely flat.

(2) The apparent temperature dependence may be due to experimental errors:-

If water vapour were present in the impurity, a positive dependence would be observed.

Alternatively the temperature dependence of the reference CO_2 may be too steep, because this could reduce

the temperature dependence of $\tau_{CO_2H_2}$, assuming no contamination of the impurity. Now, if the temperature of the apparatus were increased from room temperature whilst pumping, a large proportion of the water vapour adsorbed on the metal surfaces of the apparatus would be removed, so that contamination of the CO_2 by water vapour at high temperature would be less serious. This could not lead to too steep a temperature dependence for CO_2, and the idea must therefore be discounted. (3) The temperature dependence may be real, and be associated with the observation that H_2 and D_2 are more efficient than theory predicts. In view of (1) and (2) it would be unwise to pay too much attention to the temperature dependence in explaining the extra efficiency of H_2 and D_2.

The literature on the relative efficiencies of hydrogen, deuterium and helium for different gases shows some variation, and it should be noted that conclusions can only be drawn when V T transfer is the only physically reasonable process applicable to collisions with helium. In each example given below, Cottrell-Ream calculations have been carried out except in the case of CO, where Millikan used SSH theory.
The results are shown in Table 34.

TABLE 34 .

MOLECULE M	X	P_{10}(MX/M) THEORY	P_{10}(MX/M) EXPERIMENT	T°K	Reference.
N_2O	H_2	330	7	293	Eucken (47)
	D_2	230	13	292	Eucken (47)
	He	230	5	293	Eucken (43)
CO	H_2) Ortho)	10^6	400-4000	286°K	Millikan(48)
	H_2) Para)		1000-10,000	286°K	Millikan(48)
	D_2	90,000	26-260	286°K	Millikan(49)
	He	110,000	31-310	286°K	Millikan(49)
Cl_2	H_2	80	44	291	Eucken (18)
	He	52	38	291	Eucken (18)

N_2O: The relative efficiencies of H_2 and He are in agreement with theory, but D_2 is more efficient than either by a factor of 2. The temperature dependencies are in all cases normal except for Küchler's high temperature N_2O - He results, which show a reversed dependence.

CO: Helium and deuterium are equally efficient, but hydrogen is more efficient than the theory predicts. Moreover, para hydrogen is twice as effective as ortho.

Cl_2: Hydrogen is slightly less effective than theory.

At this point tests should be carried out to ascertain whether the theory is valid for these high speed encounters: if it is not, then an explanation of the results in terms of a new

mechanism is invalid. At sufficiently high velocities, the simple theory does give transition probabilities greater than 1, which are not physically possible. If this situation arises at velocities which correspond to a significant proportion of the velocity distribution, the theory must break down. To test this, values of the relative velocities of collision partners CO_2-D_2 and CO_2-H_2 were determined from the equation:

$$P_{10} = \frac{32\pi^4 m^2 \nu}{h \alpha^2 M} \exp\left(\frac{-4\pi^2 \nu}{\alpha v}\right)$$

for the conditions (1) $P_{10} > 1$

(2) $P_{10} > 1/2$

and assuming values of M

(3) $M = m/2$

(4) $M = m/20$

(4) being judged to be an extreme position which occurs in Methane (7). The relative number of molecules in the populations at 300 and 400°K with velocities $\geq$ those derived above were calculated from the equation :

$$N_{(\geq v)} = 1 - \operatorname{erf}\left(\frac{m}{2kt}\right)^{1/2} v$$

as in Guggenheim and Prue (51)
and are shown in Table (35).

TABLE 35.

GAS	T°K	B	P > 1		P > 1/2	
			$V_{10^{-5}}$ (cm/sec)	N_v	$V_{10^{-5}}$ (cm/sec)	N_v
CO_2H_2	300	16	4.99	0	4.01	.04%
		160	2.76	2%	2.44	2%
	400	16	4.99	.02%	4.01	.2%
		160	2.76	4%	2.44	6%
CO_2D_2	300	69	3.39	.4%	3.34	.4%
		690	2.16	6%	1.95	9%
	400	69	3.39	1%	3.34	1%
		690	2.16	11%	1.95	15%

B is the pre-exponential factor.

Extending these results to the other examples quoted here, it can be seen that the situation must improve for O_2, CO and CH_4 which have larger vibrational quanta and smaller masses, and one can conclude that the dynamics of the high velocity collisions are successfully treated by V T theory. Winter's suggestion that his observed temperature dependences in CO_2D_2 and CO_2H_2 are due to the increasing predominance of collisions which are too short in duration is not justified. This bar to the unlimited efficiency of very high speed collisions arises because the interactions between collision partners are not infinitely steep, but account is taken of this in the Landau-Teller treatment. In attempting to average their relation between transition probabilities and relative velocities over the Maxwellian distribution of velocities they reasoned that the combined effect of a steadily increasing function P_{10} (v) and the distribution

function Q (v) would lead to a fairly narrow range of effective velocities. They define the most effective velocity as

$$v^{*} = \left(\frac{4\pi^2 k t \nu}{\alpha m} \right)^{1/3}$$

If one defines a collision which is too short in duration as one which is effective over a period shorter than the vibratory period ν^{-1}, it is easily shown that at 147°C, one of Winter's working temperatures, this corresponds to a relative velocity approximately twice V^{*}, and therefore one to which little weight is given by the theory.

An explanation is now put forward to explain the extra efficiency of H_2 and D_2 over He in collision with CO_2: it takes account of the essential difference between H_2 D_2, and He, namely the presence in the former pair of internal rotational modes with rotational quanta of the same order of magnitude as the lowest vibrational modes in CO_2. These are shown in Table (36) together with ν Min for the gases discussed earlier.

TABLE 36

GAS ν MIN.	H_2								D_2							
	ORTHO 75%				PARA 25%				ORTHO 66.7%				PARA 33.3%			
	J_1	J_F	$\Delta\nu$	$\%J_1$	J_1	J_F	$\Delta\nu$	$\%J_1$	J_1	J_F	$\Delta\nu$	$\%J_1$	J_1	J_F	$\Delta\nu$	$\%J_1$
CO_2 667	1	3	594	88	0	2	356	52	0	2	179	28	1	3	298	63
N_2O 589	3	5	1069	12	2	4	828	48	2	4	417	59	3	5	536	33
CO 2143									4	6	655	13	5	7	774	4
Cl_2 557																

In purely qualitative terms the extra efficiencies of Hydrogen and deuterium could be explained in terms of vibration-rotation transfer. If part of the vibrational quantum from CO_2 were transferred into the rotational modes of deuterium, causing

say a 2 - 4 transition, then only 667 - 417 = 250 cm^{-1} of energy would be transferred to the translational modes of the gas, resulting in a more rapid de-excitation process; if a 4 - 6 transition occurred, a near resonant condition would be realised, resulting in very fast transfer. Hydrogen may be more efficient than deuterium because its lower transitions, which will be more probable due to the larger populations of 0 and 1 states, correspond to larger quanta and allow more nearly resonant transfer than the equivalent transitions in deuterium. This could also explain the CO result and also the observations by Parker (52) that H_2 is ten times more efficient than deuterium or helium for oxygens; small numbers of near resonant transitions are possible with both types of hydrogen, but the transitions in deuterium of equivalent size are unlikely because the populations of the higher rotational states required are very small. The results for chlorine and N_2O cannot be explained by this theory, but on the other hand, V T theory cannot explain the N_2O results.

The theory can be tested quantitatively for the present results, CO_2-D_2 and CO_2-He, by replacing ν = 667 cm^{-1} in the expression for the transition probability by $667 - \nu_{i(ROT)}$, the amounts of energy to be transferred to translation as a result of the transfer of ν_i into rotation in deuterium; each process is then weighted by the population of the rotational level from which the rotational transition occurs. If the scheme turns out to be more efficient than that involving ν = 667 cm^{-1}, that is, if it predicts that D_2 be more efficient than He by an amount not too different from the experimental observation, then the theory is more firmly established. Table (37) shows the rotational levels in D_2 which are well populated at 300°K, and the amounts of energy $\Delta\nu_{(TR)}$ to be transferred as a result of V - R transfer.

TABLE 37

ISOTOPE	J_i	POPULATION %	TRANSITION cm^{-1}	$\Delta\nu$ (TR) cm^{-1}
o	0	28	179	488
p	1	63	298	369
o	2	59	417	250
p	3	33	536	131
o	4	13	655	12

Now the 4 - 6 transition in ortho-deuterium is an almost exact resonance, for which there is no expression in the Cottrell-Ream paper, and it has been pointed out that the theory breaks down for small ν (53). However, SSH theory (30), which is equivalent to the Cottrell-Ream theory in its treatment of V T transfer, provides an expression for the translational factor Z (TR) for exact resonance. The transition probability per collision is given by

$$P_{10} = \frac{1}{Zo} \quad \frac{1}{Z(osc)} \quad \frac{1}{Z\ (TR)}$$

where $\frac{1}{Zo} \quad \frac{1}{Z(osc)}$ is equivalent to the pre-exponential terms in the Cottrell-Ream expression other than those given in equation (1) Page (85) and 1/Z (TR) includes the dominant exponential term exactly as in the latter. The test outlined above can therefore be carried out approximately by comparing Z (TR) for $\nu = 667\ cm^{-1}$ with the weighted mean Z(TR) for the complex scheme. For large ν , the SSH theory gives :-

$$\frac{1}{Z_{TR}} = \frac{1}{\pi^2}\sqrt{\frac{2\pi}{3}}\left[\frac{\Theta'}{\Theta}\right]^{\frac{1}{2}}\left[\frac{\Theta'}{T}\right]^{11/6}\exp\left[-\frac{3}{2}\left(\frac{\Theta'}{T}\right)^{1/3}+\frac{\Theta}{2T}\right] \qquad (1)$$

$$\Theta = \frac{h\nu}{k} \qquad \Theta' = 8y^{*3}T$$

∴ in Cottrell-Ream notation:-

$$\frac{1}{Z_{TR}} = \frac{1}{\pi^2}\sqrt{\frac{2\pi}{3}}\left[8y^{*3}\frac{kT}{h\nu}\right]\left[8y^{*3}\right]\exp\left[-3y^{*}+\frac{h\nu}{2kT}\right]$$

For exact resonance:-

$$\frac{1}{Z_{TR}} = \frac{4}{\pi^2}\frac{\Theta'T}{\Theta^2}$$

$$= \frac{4}{\pi^2}\,8y^{*3}\left(\frac{kT}{h\nu}\right)^2$$

In view of the possibility of the breakdown of expression (1) for small ν , the values of 1/Z(TR) were calculated directly for ν = 667,488,369 cm^{-1}, but the values for ν = 250, 131 cm^{-1} were interpolated from a graph of 1/Z(TR) versus ν between ν = 667,488,369 cm^{-1} and exact resonance. The results are shown in Table (38) , with the relevant populations, assuming that Ortho-D_2 is 66.7% of normal D_2, at 300, 400 and 500°K.

TABLE 38

$\Delta\nu$ (TR)	300°K		400°K		500°K	
	Z^{-1}(TR)	POPULATION %	Z^{-1}(TR)	POPULATION %	Z^{-1}(TR)	POPULATION %
667	0.83		1.08		1.61	
488	1.44	28	2.13	23	3.03	19
369	2.31	63	3.6	53	4.5	43
250	3.8	59	5.7	54	7.5	53
131	6.4	33	9.5	39	12.5	43
12	13	13	17	23	21	28

At 300°K, relative efficiencies D_2/He = 5
400°K, " " " = 6
500°K, " " " = 6

The ratios are in line with experiment, indicating that vibration-rotation transfer is a possible explanation of the experimental result. The theory also predicts a very small temperature dependence, which agrees with the magnitude if not the sign of the experimental results, which may be suspect.

DISCUSSION : PART C.

RELAXATION IN METHANE AND MIXTURES.

RELAXATION IN METHANE.

The value of 1.7 μsec. at 30°C for relaxation in methane agrees with those of Cottrell and Martin (54) and Edmonds and Lamb (55), but is shorter than that interpolated from the results of Cottrell and Matheson (3) of 1.9 μ sec. The latter result is to be preferred because great care was taken over the purification of the samples, whereas the present samples contained 0.3% hydrocarbons, mainly ethane and ethylene, which have been shown to be very efficient collision partners for a number of molecules (56). The de-activation scheme for methane has been the subject of much attention recently. A comparison of the relaxation times of CH_4 and CD_4 led Cottrell and Matheson to put forward a mechanism in which vibrational energy is transferred into rotational modes by the quickly rotating peripheral atoms, and thence to translation, rather than directly into translation:-

$$CH_4^{\divideontimes} + CH_4 \longrightarrow CH_4^{\ddagger} + CH_4^{\ddagger}$$

($\divideontimes$ and $\ddagger$ represent vibrational and rotational excitation respectively).

The idea has developed along the following lines. The Lambert-Salter plot (36) contains molecules which can be assigned to one of two groups, in the first of which a reasonable functional agreement with the Landau-Teller theory is observed. In the second group, containing molecules with low moments of inertia, no rational pattern is observed, suggesting that a different mechanism may be operative. Cottrell suggests that when molecules rotate faster than their average relative translational velocity, and have small rotational spacings, vibrational energy may be

transferred classically into the rotational modes of the collision partner of lower moment of inertia with enhanced efficiency over the usual V T process. A rational pattern is restored to the majority of the second group when a mathematical expression for the transition probability per collision is used which takes account of the peripheral velocity of the molecules. This expression appears in Cottrell's paper, and the following expression was derived by Moore (2), averaging over the angular velocity distribution. In this recent paper, Moore has extended the theory to a larger group of molecules.

$$P_{10} = \frac{1}{Zo} \left(\frac{17.1 \; I^{13/6} \; \nu^{4/3}}{d^{13/3} \; T^{1/6} \; M^{7/3} \; \alpha} \right) \exp.\left(-1.78 \left[\frac{I \nu^2}{d^2 \alpha^2 T} \right]^{1/3} \right) \exp.\left(\frac{0.719 \nu}{T}\right)$$

where I is the moment of inertia in a.m.u. A^{o2}

d is the distance of a rotating atom from the axis of rotation of the rotator

Zo is a steric factor

and the other symbols have their usual meaning.

METHANE AND ADDITIVES.

Three processes, excluding V-V processes, can be envisaged for vibrational relaxation in CH_4 - X collisions.

$$CH_4^{*} + X \longrightarrow CH_4^{\dagger} + X \quad (1)$$

$$CH_4^{\kappa} + X \longrightarrow CH_4^{\dagger} + X^{\dagger} \quad (2)$$

$$CH_4^{\kappa} + X \longrightarrow CH_4 + X \quad (3)$$

when X is O_2 or D_2 all three are theoretically possible.

when X is He, (1) and (3) are possible.

The following tests can be applied to distinguish the appropriate process for each additive.
First, process (3) can be considered using conventional V T theory to compare experimental and theoretical ratios of $P_{10}\ CH_4/P_{10}CH_4$ X, Table (39).

TABLE 39.

X	V T THEORY	EXPERIMENT.
O_2	3.5	3.5
He	0.012	2.1
D_2	0.012	0.69

Unlike the results for CO_2 and inerts, there is no constant pattern of deviation, which suggests that refinements to the V T process are unlikely to provide an explanation of the results, and that a V T process is not operative.

OXYGEN AND HELIUM.

In order to decide between process (1) and (2) the expression on Page 88 can be used for oxygen and helium. Process (1) represents the internal conversion in methane of vibrational energy into rotational energy, the collision partner providing the necessary perturbation. In methane-methane collisions vibrational energy from molecule A can flow into six rotational degrees of freedom, three in itself and three in molecule B, its collision partner. If one assumes that the probability of transfer into each degree of freedom in CH_4 is the same, and that for transfer into the rotational degrees of freedom of X it is negligible, then CH_4 - X collisions should be half as efficient as CH_4 - CH_4 collisions, corrected for differences in the sharpness of the CH_4 - X encounters. On this basis the theoretical ratios should be

$$P_{10}\left(\frac{CH_4}{CH_4X}\right)_{THEORY} \doteqdot 2 \times f\left(\frac{\alpha H - H}{\alpha H X}\right)$$

where α H X represents the sharpness of an encounter between X and the peripheral H atom. On this basis the theoretical ratios in both cases should be approximately two, in line with the experimental results.
Process (2) represents the transfer of energy into the rotational modes of X. Application of the expression on Page 88 shows that it is not significant. The theoretical ratio for CH_4 and CH_4 - O_2 was calculated using the data provided by Moore.

$M = 0.8 \qquad \alpha = 3\ A^{o\,-1} \qquad Zo = 5$

and for CH_4, $I = 3.19$ a.m.u. A^{o2}, $d = 1.02\ A^o$

for CH_4-O_2, $I = 9.68$ a.m.u. A^{o2}, $d = 0.55\ A^o$

This gives $\left(\frac{P_{10}\ CH_4}{P_{10}\ CH_4\text{-}O_2} \right)_{\text{THEORY}} \backsim 10^9$

indicating that the contribution of process (2) is not significant. One can therefore conclude that the efficiencies of helium and oxygen as collision partners for CH_4 can be explained in terms of efficient vibration - rotation transfer within the same methane molecule.

DEUTERIUM.

The results for deuterium and hydrogen (50) are not consistent with the preceding conclusion because hydrogen is more efficient than deuterium, and both are more efficient than helium. The mechanism outlined above predicts that all three be approximately equally efficient, and half as efficient as methane itself. Eucken's result for CH_4 - CO_2 (50) shows that effects other than "classical" V R transfer, possibly V V transfer, can be important. A possible scheme is:-

$$CH_4^{\kappa}\ (1306\ cm^{-1}) + CO_2 \longrightarrow CH_4 + CO_2^{\kappa}\ (1351\ cm^{-1})$$

$$CO_2^{\kappa}\ (1351) + CO_2 \longrightarrow CO_2 + Co_2^{\kappa}\ (2 \times 667)$$

$$CO_2^{\kappa}\ (667) + CH_4 \longrightarrow CO_2 + CH_4^{\dagger}$$

A process can therefore be suggested in which vibrational energy is transferred into the large rotational spacings in H_2 and D_2; the smaller amounts of energy to be transferred to translation as the result of such a process would cause an increase in the transition probability. Moreover, if this energy were transferred to translation through the rotational modes of methane, the efficiency of the overall process would be further increased. An effective collision between CH_4 and D_2 proposed here is thus a complex interaction:-

$$CH_4^{*} + \underset{J_1}{D_2} \longrightarrow CH_4^{\ddagger} + \underset{(J_1 + 2)}{D_2^{\ddagger}}$$

$$CH_4^{\ddagger} \longrightarrow \text{K.E.}$$

and would most probably be more efficient than that proposed for CH_4 - He collisions. Hydrogen would also be more efficient than deuterium (as indicated in the literature) because the rotational spacings in H_2 are larger and because the rotational levels which allow near resonant transitions are more highly populated.

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FUTURE WORK.

1. THE INTERFEROMETER.

The apparatus was not entirely satisfactory for the work on CO_2, particularly on CO_2He and CO_2D_2 due to the large absorption encountered. Three crystals broke down during the present work as a result of the prolonged application of the large voltage (10 V) required to obtain measureable resonance peaks. On the other hand the apparatus was very suitable for methane work, producing sharp resonance peaks with smaller voltages even in mixtures containing helium and deuterium. One can conclude that the apparatus can best fulfill its role as a routine measuring device for gases where ν Min is of the order of 1000 cm^{-1}. It is capable of a high degree of accuracy when gases are used in which only classical absorption is important, and could therefore be used to measure "S" values, which are related to the second virial coefficient through the relation on Page 11.

2. VIBRATION-ROTATION TRANSFER.

Further experimental and theoretical work is required on the problem of the D_2 - He ratio with regard to two variables, the mismatch between ν vib and ν rot, and the populations of rotational levels in D_2; the former should be on the broadest possible basis, in order to establish a general pattern of behaviour; otherwise the theory possesses only the limited status of a special effect. Temperature dependence studies may not provide significant information when ν Min is small, but when ν Min is approximately 1000 cm^{-1} or more, as in O_2, where at room temperature D_2 is no more efficient than He, an increase in the efficiency of D_2 over He as the temperature increases would be evidence in favour of V R transfer. A rigorous theoretical treatment of the problem is essential to the future of the theory.

3. METHANE AND MIXTURES.

A more thorough investigation of the effect of inert gases on relaxation in methane is required to test the conclusion reached in Part C that collision partners simply provide the necessary perturbation for the transfer of vibrational energy into rotational energy in the same methane molecule. If $P_{10}CH_4 - X$ did not vary for X = He, Ne, Ar, Xe, then the idea would be very firmly established. A parallel study using CD_4 and inerts would also be useful, and would incidentally test the conclusion that V T transfer is not directly operative: if $P_{10}(CH_4X/CD_4X)$ for different X were approximately the value found for the pure gases, V-R transfer would be further proved and V-T transfer disproved, because if V-T transfer were operative, the ratio would revert to that predicted by conventional V-T theory for reduced collision masses less than or equal to those of the pure gases.

REFERENCES.

1.	LANDAU, L., TELLER, E.	Phys.Zeit.Sowjetunion	1936	10	34
2.	MOORE, C.B.,	J. Chem.Phys.	To be published.		
3.	COTTRELL, T.L.,MATHESON,A.J.	Trans.Faraday Soc.	1962	58	2336
4.	MILLIKAN, R.C.,WHITE, D.R.,	J.Chem.Phys.	1963	39	3209
5.	HUDSON, G.H., McCOUBREY,J.C. UBBELOHDE, A.R.,	Proc.Roy.Soc.	1961	264A	289
6.	TANCZOS, F.,	J.Chem.Phys.	1956	25	439
7.	COTTRELL, T.L., REAM, N.,	Trans.Faraday Soc.	1955	51	1453
8.	LAMBERT, J.D., PARKS-SMITH, D.G., STRETTON, J.L.,	Proc.Roy.Soc.	1965	282A	380
9.	ROBERTS, J.K.,	"Heat and Thermodynamics"	(Blackie,London 1954)		
10.	LAMBERT, J.D., ROWLINSON,J.S.	Proc.Roy.Soc.	1951	204A	424
11.	HIRSCHFELDER, J.O., CURTISS, C.F., BIRD, R.B.,	"Molecular Theory of Gases and Liquids"	(Wiley, New York 1954)		
12.	FARMER, P.J.,	"Machinery"	1958	932	
13.	MATHESON, A.J.,	Ph.D. Thesis, Edinburgh 1962.			
14.	BLYTHE, A.R.,	Ph.D. Thesis, Edinburgh 1962.			
15.	KAYE, G.W.C., SHERRATT, G.G.	Proc.Roy Soc.	1933	141A	123
16.	GRABAU, M.,	J.Acoust. Soc. Amer.	1933	5	1
17.	STEWART, E.S.,STEWART, J.L.,	J.Acoust. Soc. Amer.	1952	24	23
18.	EUCKEN, A., BECKER, R.,	Z.Phys.Chem.	1934	27B	219
19.	KNOETZEL, H., KNOETZEL,L.,	Ann.Physik.	1948	2	393
20.	HOLBORN, L., OTTO, J.,	Z.Phys.	1925	33	1.
21.	PIELEMEIER, W.H., SAXTON, H.L., TELFAIR, D.,	J.Chem.Phys.	1940	8	106
22.	HERZBERG, G.,	"Infra-Red and Raman Spectra"	(Van Nostrand Princeton 1945)		
23.	MICHELS, A., MICHELS, C.,	Proc.Roy.Soc.	1936	153A	201
24.	MacCORMACK, K.E., SCHNEIDER, W.G.,	J.Chem.Phys.	1950	18	1269

25.	COTTRELL, T.L., HAMILTON, R.A.,	Trans.Faraday Soc.	1956	52	156
26.	STEWART, E.S., STEWART, J.L.,	J.Acoust.Soc.Amer.	1952	24	194
27.	CLUSIUS, K., RICCOBINI, L.,	Z.Phys.Chem.	1938	38B	81
28.	COTTRELL, T.L.,McCOUBREY, J.C.,	"Molecular Energy Transfer in Gases" (Butterworth,London,1961)			
29.	SLUIJTER, C.G.,	Ph.D. Thesis (Leiden) 1964			
30.	SCHWARTZ, R.N., SLAWSKY, Z.I., HERZFELD, K.F.,	J.Chem. Phys.	1952	20	1591
31.	deWETTE,F.W., SLAWSKY, Z.I.,	Physica.	1954	20	1169
32.	SHIELDS, F.D.,	J.Acoust.Soc.Amer.	1959	31	248
33.	ANGONA, F.A.,	J.Acoust.Soc.Amer.	1953	25	1116
34.	BUSCHMANN, K.F., SCHÄFER, K.,	Z.Phys.Chem.	1941	50B	73
35.	HOLMES, R.,	J.Chem. Phys.	1964	41	2955
36.	LAMBERT, J.D., SALTER, R.,	Proc.Roy.Soc.	1959	253A	277
37.	KNUDSEN, V.O., FRICKE, E.,	J.Acoust.Soc.Amer.	1940	12	255
38.	KÜCHLER, L.,	Z.Phys.Chem.	1938	41B	199
39.	KNESER, H.O., ROESLER, H.,	Acustica	1959	9	224
40.	BAUER, H-J., LISKA, E.,	Z.Phys.	1964	181	356
41.	WALLMANN, M.H.,	Ann.Phys.Lpzg.	1934	21	671
42.	LEGVOLD, S., AMME, R.,	J.Chem. Phys.	1960	33	91
43.	EUCKEN, A. NÜMANN, E.,	Z.Phys.Chem.	1937	36B	163
44.	HERSCHBACH, D.R., MARTIN,R.M., FLUENDY, M.A.D.,	J.Chem.Phys. To be published.			
45.	McCOUBREY, J.C., MILWARD, R., UBBELOHDE, A.R.,	Trans.Faraday Soc.	1961	57	1472
46.	WINTER, T.G.,	J.Chem.Phys.	1963	38	2761
47.	EUCKEN, A., JAACKS, H.,	Z.Phys.Chem.	1935	30B	85
48.	MILLIKAN, R.C., OSBURG, L.A.,	J.Chem.Phys.	1964	41	2196
49.	MILLIKAN, R.C., WHITE, D.R.,	J.Chem.Phys.	1963	38	2855
50.	EUCKEN, A., AYBAR, S.,	Z.Phys.Chem.	1940	46B	195
51.	GUGGENHEIM,E.A., PRUE, J.E.,	"Physico-Chemical Calculations" (North-Holland,Amsterdam,1956)			

52. PARKER, J.G., J.Chem.Phys. 1961 34 1763

53. HERZFELD, K.F., LITOVITZ,T.A.,"Absorption and Dispersion of Ultrasonic Waves" (Academic Pres New York & London 1959)

54. COTTRELL, T.L., MARTIN, P.E.,Trans.Faraday Soc. 1957 53 1157

55. EDMONDS, P.D., LAMB, J., Proc.Phys.Soc., London 1958 72 940

56. ARNOLD, J.W., McCOUBREY,J.C., UBBELOHDE, A.R., Trans.Faraday Soc. 1957 248A 445

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